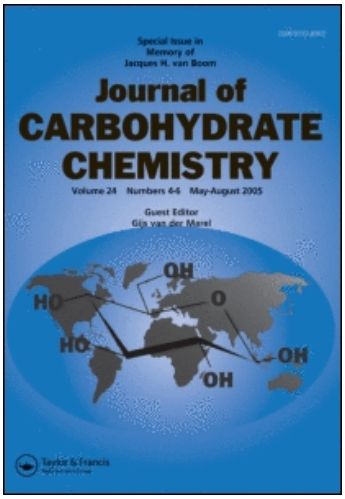


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# Metal-Graphite Reagents in Carbohydrate Chemistry, VII. Fragmentation of 0-Alkylidene-Deoxy Halo Sugars.

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# METAL-GRAPHITE REAGENTS IN CARBOHYDRATE CHEMISTRY, VII.[1]

## FRAGMENTATION OF O-ALKYLIDENE-DEOXY HALO SUGARS.

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ABSTRACT

Contrary to the methods previously described, treatment with zinc/-silver-graphite or potassium-graphite laminate ($C_8K$) of the di-O-isopropylidene derivatives of 1-deoxy-1-halo-ß-D-fructopyranose, 1-deoxy-1-halo-α-L-sorbofuranose, 6-deoxy-6-iodo-α-D-galactopyranose, and 3-deoxy-3-iodo-α-D-glucofuranose resulted in the high yield formation of the respective unsaturated sugar derivatives by fragmentation with loss of one of the acetal groups.

## INTRODUCTION

The increasing interest in cyclic and acyclic unsaturated sugar derivatives such as glycals,[3] 6-deoxy-hex-5-enopyranosides,[4] and particularly 4,5-dideoxy-aldopent-4- and 5,6-dideoxy-aldohex-5-enoses [5] as educts for carbohydrate and other natural product syntheses has recently lead to substantial improvements in the preparation of these types of synthons.[6-11] Thus, new and quite generally applicable glycal syntheses[6,7] as well as chemo- and regioselective elimination reactions of various deoxyhalo sugars were described,[8,9] for which both zinc/silver-graphite and potassium-graphite laminate ($C_8K$), because of their complementary behaviour, proved to be the reagents of choice.

However, there are yet no plausible explanations regarding either the mechanism of activated zinc-induced fragmentations of deoxyhalo sugars or glycosyl halides or the totally different behaviour of $C_8K$

towards the former educts as compared to any zinc reagent.[8] To complicate matters this result on the other hand is inconsistent with the fragmentations of glycosyl halides both by zinc/silver-graphite and $C_8K$ with the latter only being more reactive.[6-8]

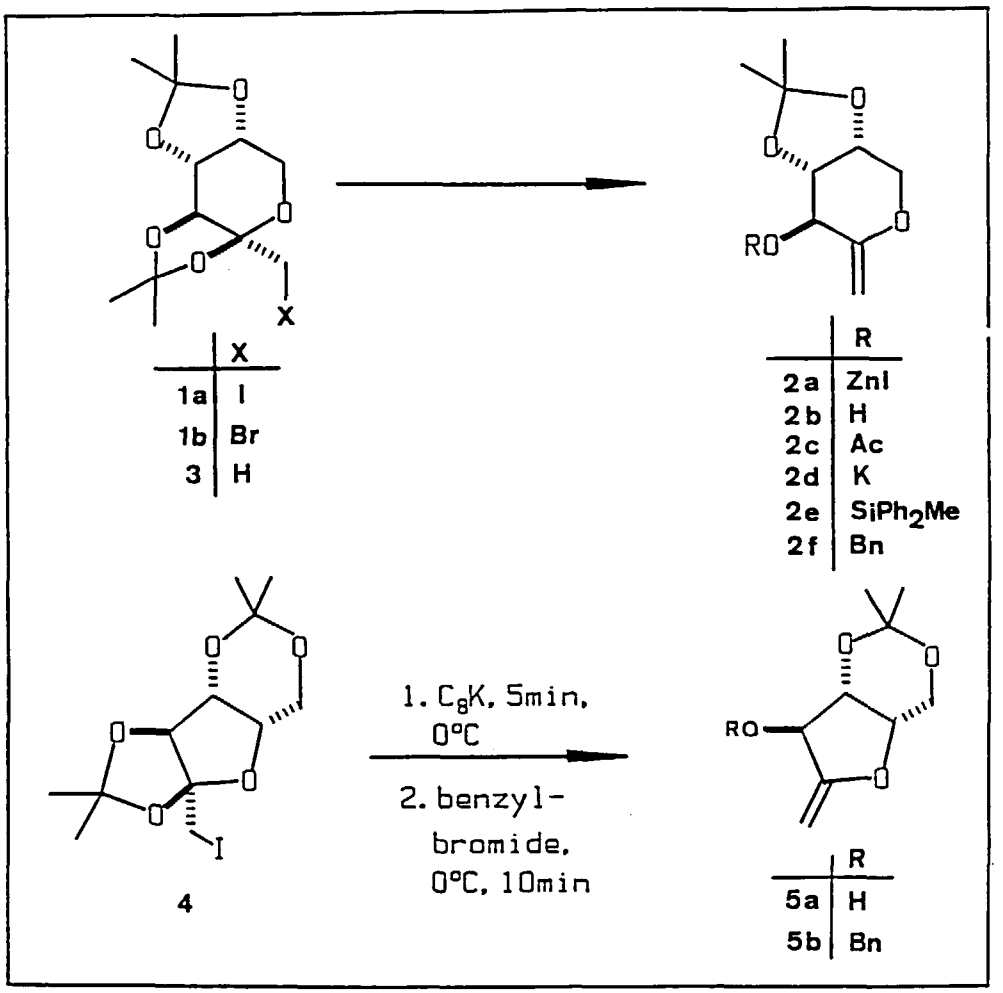
In view of this puzzling situation further investigations were called for. This paper describes the results of fragmentation reactions of a number of selected *O*-alkylidene-deoxyhalo sugars, extending the applicability of both zinc/silver-graphite and $C_8K$ in carbohydrate transformations.

## RESULTS AND DISCUSSION

For the substitution of each of the primary hydroxyl groups by iodine in the di-*O*-isopropylidene-ß-D-fructopyranose, -α-L-sorbofuranose, and -α-D-galactopyranose, the iodine/triphenylphosphine/imidazole reagent was used;[12] the reactions, however, proceeded by a considerably higher rate than originally described. Both the 1-bromo-1-deoxy-2,3;4,5-di-*O*-isopropylidene-ß-D-fructopyranose (1b)[13] and the 3-deoxy-3-iodo-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (8)[9,14] were prepared by reactions of their respective O-sulfonyl derivatives with the appropriate halide ion, the latter compound (8) from 1,2;5,6-di-*O*-isopropylidene-3-O-triflyl-α-D-allofuranose.

In view of the results of our previous investigations of zinc/silver-graphite- and $C_8K$-induced elimination reactions,[6-9] the derivatives of 1-deoxy-1-halo-ß-D-fructopyranose (1) and 1-deoxy-1-iodo-α-L-sorbofuranose (4) independent of the reagent can only be subject to fragmentations, although each in two different directions. The products of the corresponding reactions of the 6-deoxy-6-iodo-α-D-galactopyranose (6) and 3-deoxy-3-iodo-α-D-glucofuranose derivative (8), however, are dependent on the respective reagent used, suffering either fragmentation or dehydrohalogenation as recently demonstrated with the latter of these educts.[8] The results now obtained are quite noteworthy.

Treatment of 1a with zinc/silver-graphite in THF as described for various other deoxyhalo sugars[8] resulted only in the elimination of its 2,3-O-isopropylidene group without effecting the tetrahydropyran ring thereby forming the unstable enol ether 2b, isolated as its 3-O-acetyl derivative 2c. Interestingly, under the same conditions 1b gave the 1-deoxy-2,3;4,5-di-O-isopropylidene-ß-D-fructopyranose 3,[15] also resulting from 1a but at much lower temperature. While other fragmentations with the same reagent were recently found to be independent of the kind of halogen,[8] this new result must presently remain unexplained.




SCHEME I

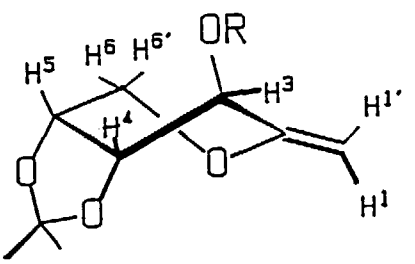



FIG.1. Conformation of 3-O-protected 2,6-anydro-1-deoxy-4,5-O-isopropylidene-D-arabino-hex-1-enitols (2).

However, in agreement with glycosyl halide fragmentations, independent of both the temperature and the kind of the deoxyhalo function, $C_8K$ uniformly produces only 2 from either 1a or 1b . The immediate formation of the potassium alkoxide 2d is an additional advantage of this reagent, allowing direct *in situ* O-protection with various electrophiles.[7]

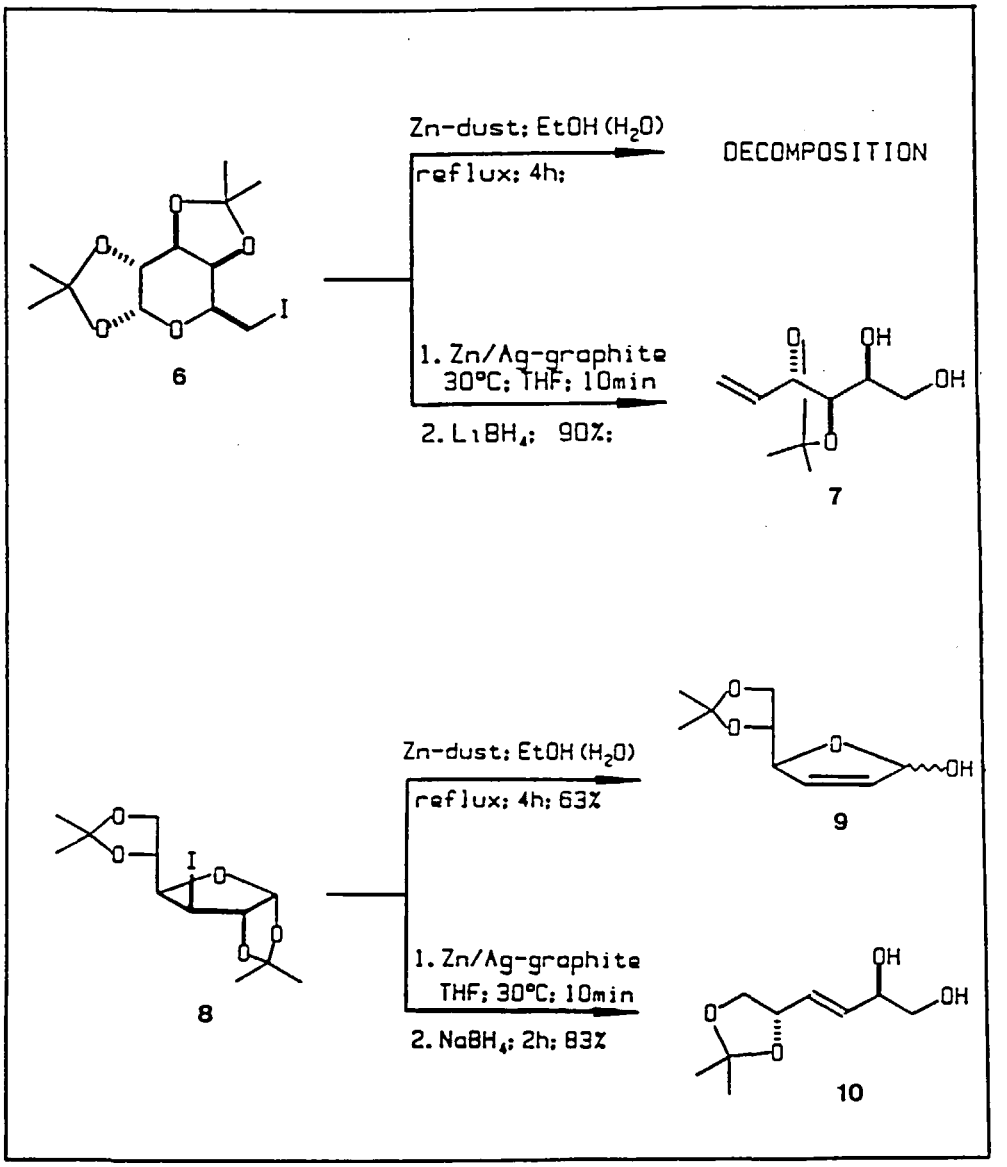
Compound 2c, most likely to escape the steric proximity of the 3-hydroxyl and the vinyl groups, adopts a twist conformation of the tetrahydropyran ring, forcing the oxygen atom into an axial position. This structure is obviously responsible for the limited stability of 2, the benzyl ether 2f of which, as compared to the acetyl and methyldiphenylsilyl derivatives 2c and 2e is quite rapidly hydrolyzed to afford 3-O-benzyl -deoxy-4,5-O-isopropylidene-α,ß-D-fructopyranose.

In accordance with the foregoing results, treatment of 4 with $C_8K$ at temperatures between 0 °C and 30 °C invariably gives the expected product 5a which was O-benzylated (5b) *in situ* to simplify isolation. Compared to 2f the resulting 2,5-anhydro-1-deoxy-3-O-benzyl-4,6-O-isopropylidene-L-*xylo*-hex-1-enitol 5b is quite stable to hydrolysis.

As demonstrated by the reactions of glycosyl halides and various deoxyhalo sugar derivatives, including the compounds 1 and 4 described above, only the fragmentations in aprotic solvents by highly active zinc/silver-graphite or $C_8K$ are equally efficient and generally applicable.[6-9] The reactions of 8 and 6 are shown to be additional examples for the superiority of these reagents over the conditions originally described.[11] Thus, while treatment of the latter compound with activated zinc in aqueous ethanol[11] leads to complete destruction, zinc/silver-graphite causes a regular fragmentation affording a di- or oligomeric product, which after borohydride reduction gave 5,6-dideoxy-3,4-O-isopropylidene-L-*arabino*-hex-5-enitol (7) as the only compound. On the other hand, the 2,3-dideoxy-5,6-O-isopropylidene-D-*erythro*-hex-2-enofuranose (9), obtained from 8 by conventional conditions, differs from the product (10)[8] of the zinc/silver-graphite fragmentation and was found to have resulted from a consecutive allylic rearrangement. NMR-analysis showed the formation of the same intermediate in both procedures.

## EXPERIMENTAL

General. Reactions were performed in THF (Aldrich) distilled over $LiAlH_4$ before use. For all $C_8K$ preparations LONZA HSAG9 graphite was




SCHEME II

used, but any other kind of graphite proved to be equally suitable. TLC was performed on precoated silica gel plates (MERCK 60 F-254) and column chromatography on silica gel (MERCK 230-240 mesh). For $^{1}H$ and $^{13}C$ NMR spectroscopy a BRUKER MSL 300 instrument was used with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Optical rotations were measured in $CH_2Cl_2$ on a JASCO DIP 370 polarimeter.

**Fragmentation Reactions by Zinc/Silver-Graphite. General Procedure.** 5.4 Mmol of compounds 1a, 1b, 6, and 8 each in THF (20 mL) were added to suspensions of zinc/silver-graphite (15 mmol)[6,8] in THF (30 mL) with stirring under argon at the respective temperatures given in the Table. After completion of the reactions (c.f. Table) the mixtures were filtered and the solutions worked-up as follows:

(a) To the solution resulting from 1a pyridine (20 mL), 4-dimethylaminopyridine (0.2 g, 1.6 mmol) and acetic anhydride (1.10 g, 10.8 mmol) were added and the mixture stirred for 12 h at ambient temperature. After removal of the solvents by repeated azeotropic distillation with toluene (100 mL) the residue was chromatographed (eluent: toluene / ethyl acetate = 15 / 1) yielding 2c (70%).

(b) Product 3 resulting from 1a at -30 °C and 1b at 30 °C was simply obtained by evaporation of the THF and column chromatography using toluene / ethyl acetate = 10 / 1 as eluent (yields c.f.Table).

(c) The solutions of the primary, unstable reaction products resulting from educts 6 and 8 were treated with $LiBH_4$ (0.22 g, 10 mmol), concentrated and chromatographed (toluene / ethyl acetate = 15 / 1) affording products 7 and 10 in yields of 90% and 83% , respectively.

**Fragmentations Reactions by $C_8K$. General Procedure.** 5 Mmol each of the solutions of 1a, 1b and 4 were added to suspensions of $C_8K$ (10 mmol) in THF (30 mL) with stirring under argon at 0 °C; After completion of the fragmentations the respective electrophiles (10 mmol) (c.f. Table) were introduced into each of the suspensions which were stirred under argon for the appropriate period, filtered, the filtrates concentrated and the residues sujected to column chromatography (toluene / ethyl acetate = 15 / 1) giving 2c, 2e, 2f and 5b, respectively, in yields shown in the Table.

**2,6-Anhydro-3-O-acetyl-1-deoxy-4,5-O-isopropylidene-D-arabino-hex-1-enitol (2c).** Oil; $[\alpha]_D^{20}$ -35.8° (c 4); IR: 1650cm$^{-1}$(m); $^{1}H$ NMR: 5.36 (dd, 1H, H-3, $J_{3,4}$=2.6, $J_{1a,3}$=1); 4.54 (d, 1H, H-1a); 4.42 (ddd, 1H, H-5, $J_{4,5}$=7.5, $J_{5,6a}$=1.7, $J_{5,6b}$=1.9); 4.34 (d, 1H, H-4); 4.30 (s, 1H, H-1b); 4.21 and 4.12 (d-AB-system, 2H, H-6a, H-6b, $J_{A,B}$=12.7); 2.10 (s, 3H, $CH_3$-

TABLE. Zn/Ag-graphite and $C_8K$-induced fragmentation reactions

| Educt | Reagent[a] | Electrophile | Conditions[c] | Yield |
|---|---|---|---|---|
| 1a | Zn/Ag-graphite | $Ac_2O$[b] | 30 °C(10min)/25°C(12h) | 2c(70%); 3(5%) |
| 1a | Zn/Ag-graphite | $Ac_2O$[b] | -30 °C(10min)/25°C(12h) | 2c(8%); 3(79%) |
| 1b | Zn/Ag-graphite | --- | 30 °C(10min) | 3(80%) |
| 1a | $C_8K$ | $Ac_2O$ | 0 oC(10min)/0 °C(20min) | 2c(82%) |
| 1b | $C_8K$ | $Ac_2O$ | 0 °C(20min)/0 °C(20min) | 2c(80%) |
| 1a | $C_8K$ | $Ph_2MeSiCl$ | 0 °C(10min)/0 °C(10min) | 2e(88%) |
| 1a | $C_8K$ | BnBr | 0 °C(1omin)/25 °C(30min) | 2f(72%) |
| 4 | $C_8K$ | BnBr | 0 °C(10min)/25 °C(15min) | 5b(68%) |
| 6 | Zn/Ag-graphite | --- | 30 °C(10min) | 7(90%)[d] |
| 8 | Zn-dust[e] | --- | 80 °C(4h) | 9(63%) |
| 8 | Zn/Ag-graphite | --- | 30 °C(10min) | 10(83%)[d] |

a. in anhydrous THF unless stated otherwise

b. with pyridine/dimethylaminopyridine as base

c. refers to reaction temperature(reaction time)/reaction temperature(reaction time) after addition of electrophile

d. using $LiBH_4$ to reduce the crude $\alpha$-hydroxy aldehyde

e. in aqueous ethanol

COOR); 1.47, 1.35 (s, 3H each, Me-isopropylidene); $^{13}C$ NMR: 169.03 (-COOR); 151.91 (C-2); 110.30 (=C= isopropylidene); 93.63 (C-1); 72.47, 71.91, 70.77 (C-3, C-4, C-5); 64.25 (C-6); 26.41, 24.53 (Me-isopropylidene); 21.23 ($CH_3COOR$);

2,6-Anhydro-3-O-(methyldiphenylsilyl)-4,5-O-isopropylidene-D-arabino-hex-1-enitol (2e). Oil; $[\alpha]_D^{20}$ -25.1° (c 8.3); IR: 1645 $cm^{-1}$ (m); $^1H$ NMR: 7.44-7.77 (m, 10H, Ph-); 4.82 and 4.23 (AB-system, 2H, H-6a, H-6b, $J_{A,B}$=12.1); 4.55 (s, 1H, H-1a); 4.51 and 4.48 (d-AB-system, 2H, H-4, H-5, $J_{4,5}$=9.2; $J_{3,4}$=2.3); 4.07 (s, 1H, H-1b); 1.58, 1.45 (s, 3H each, Me-isopropylidene); 0.88 (s, 3H, Me-Si); $^{13}C$ NMR: 155.79 (C-2); 135.01, 134.86, 130.64, 128.59 (-Ph); 110.34 (=C= isopropylidene); 91.70 (C-1); 75.52, 73.08, 71.08 (C-3, C-4, C-5); 64.70 (C-6); 26.95, 25.1= (Me-isopropylidene); -1.65 (Me-Si);

2,6-Anhydro-3-O-benzyl-1-deoxy-4,5-O-isopropylidene-D-arabino-hex-1-enitol (2f). Oil; $[\alpha]_D^{20}$ -27° (c 4); IR: 1655 $cm^{-1}$ (m); $^1H$ NMR (60MHz): 7.2 (bs, 5H, Ph-); 4.77 (s, 1H, H-1a); 4.63 and 4.53 (AB-system, 2H, $-OCH_2Ph$, $J_{A,B}$=12); 4.30 (s, 1H, H-1b); 4.40-4.50 (m, 4H, H-3, H-4, H-5, H-6a); 4.08 (d, 1H, H-6b, $J_{5,6b}$=2); 1.90 , 1.75 (s, 3H each, Me-isopro pylidene); $^{13}C$ NMR: 154.56 (C-2); 137.64, 128.96, 128.81 (Ph-); 110.26 (=C= isopropylidene); 92.10 (C-1); 73.94, 72.80, 70.48, 70.34 (C-3, C-4, C-5, $-OCH_2Ph$); 61.06 (C-6);

1-Deoxy-2,3;5,6-di-O-isopropylidene-ß-D-fructopyranose (3). Oil; $[\alpha]_D^{20}$ -14.8° (c 15) (-10.4, c 3, $CHCl_3$, ref.15); $^1H$ NMR: 4.50 (dd, 1H, H-4, $J_{3,4}$=2.5, $J_{4,5}$=4.0); 4.17 (dd, 1H, H-5, $J_{5,6a}$=1.9, $J_{5,6b}$=0.8); 4.03 (d, 1H, H-3); 3.80 and 3.59 (d-AB system, 2H, H-6a, H-6b, $J_{A,B}$=13.3); 1.48, 1.43, 1.39, 1.27, 1.26 (s, 3H each, H-1, Me-isopropylidene); $^{13}C$ NMR: 109.10 , 107.88 (=C= isopropylidene); 102.78 (C-2); 74.13, 70.94, 70.85 (C-3, C-4, C-5); 61.28 (C-6); 27.50, 26.49, 26.09, 24.93, 24.39 (C-1, Me-isopropylidene);

2,5-Anhydro-1-deoxy-3-O-benzyl-4,6-O-isopropylidene-L-xylo-hex-1-enitol (5b). Oil; $[\alpha]_D^{20}$ 4.8° (c 9.1); IR: 1670 $cm^{-1}$ (s); $^1H$ NMR: 7.32 (bs, 5H, Ph-); 4.71 and 4.46 (AB-system, 2H, $-OCH_2Ph$); 4.65 (s, 1H, H-1a); 4.31 (s, 1H, H-1b); 4.21 (dd, 1H, H-5, $J_{4,5}$=1.9, $J_{5,6a}$=1.5); 4.15 (s, 1H, H-3); 4.05 (d, 2H, H-6a, H-6b); 1.42, 1.35 (s, 3H each, Me-isopropylidene); $^{13}C$ NMR: 160.15 (C-2); 137.75, 129.12, 128.94, 128.56 (Ph-); 97.46 (=C= isopropylidene); 86.00 (C-1); 82.85 (C-3); 74.47, 73.00 (C-4, C-5); 70.21 ($-OCH_2Ph$); 69.29 (C-6); 28.72, 19.31 (Me-isopropylidene);

5,6-Dideoxy-3,4-O-isopropylidene-L-arabino-hex-1-enitol (7). Oil; $[\alpha]_D^{20}$ 23.6° (c 6); IR: 3650-3100 $cm^{-1}$ (bs); $^1H$ NMR: 5.93 (d-X part of an ABX system, 1H, H-5, $J_{4,5}$=8.4, $J_{5,6a}$=11.8, $J_{5,6b}$=17.7); 5.28 (d-AB part of the ABX system, 2H, H-6a, H-6b, $J_{A,B}$=16); $^4J_{4,6a}$=1.2); 4.54 (ddd, 1H, H-4, $J_{3,4}$=7.0); 4.12 (dd, 1H, H-3, $J_{2,3}$=4.6); 3.61 (m, 3H, H-2, H-1a, H-1b); 3.20, 3.03 (bs, 1H each, -OH, disappears on addition of $D_2O$); 1.49, 1.32 (s, 3H each, Me-isopropylidene); $^{13}C$ NMR: 134.01 (C-5); 119.62 (C-6); 108.98 (=C= isopropylidene); 79.09, 77,90, 70.22 (C-2, C-3, C-4); 63.99 (C-1); 27.42, 25.16 (Me-isopropylidene);

2,3-Dideoxy-5,6-O-isopropylidene-α,ß-D-erythro-hex-2-enofuranose (9). Oil; $[\alpha]_D^{20}$ -40.3° (c 2) (-45°, ref. 10c); IR: 3700-3100 $cm^{-1}$ (bs); $^1H$ NMR: 7.41 (s, 1H, H-3); 6.35 (bs, 2H, H-1, H-2, $J_{1,2}$<1); 5.09 (dd, 1H, H-5, $J_{5,6a}$=$J_{5,6b}$=6.7); 4.22 and 4.10 (d-AB system, 2H, H-6a, H-6b, $J_{A,B}$=7); 2.20 (bs, 1H, -OH, disappears on addition of $D_2O$); 1.50, 1.45 (s, 3H each, Me-isopropylidene); $^{13}C$ NMR: 143.12 (C-3); 110.55 (C-2); 110.17 (=C= isopropylidene); 108.49 (C-1); 71.59, 66.50 (C-4, C-5); 66.19 (C-6); 26.61, 26.18 (Me-isopropylidene);

3,4-Dideoxy-5,6-O-isopropylidene-D-erythro-hex-3-enitol (10). Oil; $[\alpha]_D^{20}$ 31.3° (c 7.5); IR: 3700-3080 $cm^{-1}$ (bs); $^1H$ NMR: 5.85 (dd, 1H, H-4, $J_{3,4}$=11.2, $J_{4,5}$=6.0); 5.55 (dd, 1H, H-3, $J_{2,3}$=8.1); 4.47 (ddd, 1H, H-2, $J_{1a,2}$=7.1, $J_{1b,2}$=5.8); 4.26 and 4.13 (d-AB system, 2H, H-1a, H-1b, $J_{A,B}$=13.2); 4.07 and 4.03 (d-AB-system, 2H, H-6a, H-6b, $J_{A,B}$=6.3, $J_{5,6a}$= $J_{5,6b}$=1.3); 3.93 (ddd, 1H, H-5); 3.02, 2.40 (bs, 1H each, -OH, disappears on addition of $D_2O$); 1.44, 1.36 (s, 3H each, Me-isopropylidene); $^{13}C$ NMR: 132.62, 131.02 (C-3, C-4); 109.79 (=C= isopropylidene); 78.14, 68.31, 66.07, 58.57,(C-1, C-2, C-5, C-6); 26,53, 25.22 (Me-isopropylidene);

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