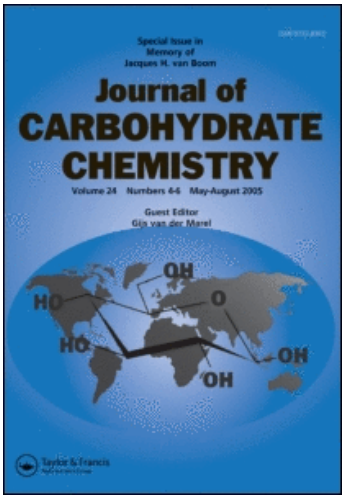

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A Simple and Efficient New Glycal Synthesis

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A SIMPLE AND EFFICIENT NEW GLYCAL SYNTHESIS

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ABSTRACT

Potassium-graphite laminate (C_8K) in oxolane almost instantaneously converts O-alkyl and O-alkylidene pyranosyl and furanosyl chlorides under extremely mild conditions and in high yields into pyranoid and furanoid glycals, which in the presence of an additional mole of C_8K, are efficiently O-alkylated or O-silylated in easily conducted one-pot reactions.

INTRODUCTION

The widespread use of variously protected glycals[1] [1,4-(1,5)-anhydro-2-deoxy-pent-(hex)-1-enitols] in syntheses of carbohydrate and non-carbohydrate products such as C-nucleosides,[2] ionophores,[3] leucotrienes,[4] heteroprostanoids,[5] 2-deoxy-2-fluoro-,[6] and 2-amino-2-deoxy sugars[7] has aroused considerable interest recently in equally simple and efficient procedures for their preparation. The long-known Fischer-Zach method because of its aqueous acidic conditions was found to be inadequate for the synthesis of furanoid glycals,[8] which show a pronounced tendency for allylic rearrangements.[8,9] Modern procedures invariably use anhydrous neutral or basic conditions.[3,5,7,9-13] Among these methods metal-induced fragmentations of 2,3-O-alkylidene glycosyl halides are preferred, providing 3-O-unprotected glycals for the subsequent reaction with various protecting agents.[3,10,11,12] The reagents found so far that foster glycal formation are lithium[3,10] and, under totally different conditions, highly reactive zinc.[12]

Glycal formation is brought about in moderate yields only with sodium naphtalide.[11] Moderately activated zinc or zinc/copper couple is applicable to 2-O-sulfonyl iodides only,[13] which are prepared in situ from the corresponding chlorides. This latter method does not form partially unprotected glycals, which is a limitation in natural product syntheses.

RESULTS AND DISCUSSION

During the course of a comprehensive investigation of reductions by highly reactive metal-graphite combinations[12,14,15] zinc/silver-graphite in oxolane was recently found to reduce O-alkylidene furanosyl as well as O-acetyl pyranosyl halides with the formation of furanoid and pyranoid glycals in high yields and purity.[12] This was the first non-aqueous Fischer-Zach type glycal synthesis under neutral conditions to be described. While this method as all other metal-induced reductions does not provide O-acylated furanoid glycals, several advantages over well-accepted procedures are worth mentioning:

1. Formation of by-products due to displacement of halide by hydride anion[3] is not observed.
2. Zinc/silver-graphite can be employed in nearly equimolar amounts and work-up of the reaction mixtures is quite simple.
3. The method is compatible with O-acyl as well as O-benzyl groups.

However, all presently known glycal syntheses suffer from specific shortcomings with respect to the accessability of educts, protective group compatibility, reagent preparation and work-up, rate of reaction, yield and purity of the products or consecutive reactions of the glycals.

Although the utility of potassium-graphite laminate (C_8K)[15] was assumed to be quite limited in reactions with highly functionalized educts because of its indiscriminating reactivity,[16] it turned out to be the reagent of choice for the synthesis of glycals from O-alkyl- and O-alkylidene glycosyl halides. Various aspects demonstrate the improvements in this new glycal synthesis:

1. Even at -78°C elimination reactions proceed with unprecedented high rates demonstrating the extreme degree of reactivity of potassium in graphite as compared to even zinc/silver-graphite[12] or unsupported potassium.[11]
2. Yields of the glycals are at least as high as with the most efficient procedures[3,10,12] presently known, and the purity of the products is superior to that from Ireland's method.[3,10]
3. The 3-O-unprotected furanoid glycals can either be easily isolated or, with an additional mole of C_8K, the intermediate potassium alcoholates are rapidly alkylated or silylated without isolation of the intermediates in one-pot processes. This not only greatly simplifies the formation of differentially protected furanoid glycals,[17] but also gives high overall yields. While the lithium in ammonia procedure[3,10] does not allow such one-pot reactions[18] the previously reported 3-O-alkylations or 3-O-silylations of this kind of glycals are quite slow.[4,6,17]
4. Unlike any other reagent C_8K eliminates 2-benzyloxy groups in per-O-benzylated glycosyl halides leaving all others uneffected. This way the first direct formation of 3,4,6-tri-O-benzyl-D-glucal[19] (13) was accomplished.
5. All reactions can be performed in oxolane and work-up is simply achieved by filtration of insolubles.

While the major improvements of the zinc/silver-graphite induced glycal synthesis rest in its ability to form furanoid and O-acylated pyranoid glycals,[12] those of C_8K consist of an enhanced reactivity allowing efficient substitution of 3-O-unprotected furanoid glycals as well as in the fragmentation of 2-O-alkyl glycopyranosyl halides. With these specific characteristics these procedures are complementary to each other and allow the synthesis of various but not of 3-O-acylated furanoid glycals.

EXPERIMENTAL

General. Reactions were performed in oxolane (MERCK puriss.pa.) distilled over $LiAlH_4$ before use. For all C_8K preparations LONZA HSAG 9 graphite was used, but any other kind of graphite proved to be equally suitable. TLC was

TABLE. Formation of 3-O-unprotected and 3-O-protected glycals by C_8K in oxolane.

EDUCT	ELECTROPHILE[a]	PRODUCT	REACTION CONDITIONS[b]	YIELD[c]
(1)	H_2O[d]	(2)	5 min; 0°C	94%
(1)	H_2O[d]	(2)	10 min; -20°C	94%
(1)	H_2O[d]	(2)	10 min; -78°C	96%
(1)	Benzyl bromide	(3)	5/60 min; 0°C	84%
(1)	$ClCH_2OCH_3$	(4)	5/30 min; 0°C	77%
(1)	$Ph_2MeSiCl$	(5)	5/15 min; 0°C	90%
(1)	(1)	(6)	5/90 min; 0°C	86%
(7)	H_2O[d]	(8)	10 min; -78°C	92%
(7)	Benzyl bromide	(9)	5/60 min; 0°C	86%
(7)	$ClCH_2OCH_3$	(10)	5/20 min; 0°C	80%
(7)	$Ph_2MeSiCl$	(11)	5/15 min; 0°C	90%
(12)	-------	(13)	10 min; 0°C	88%

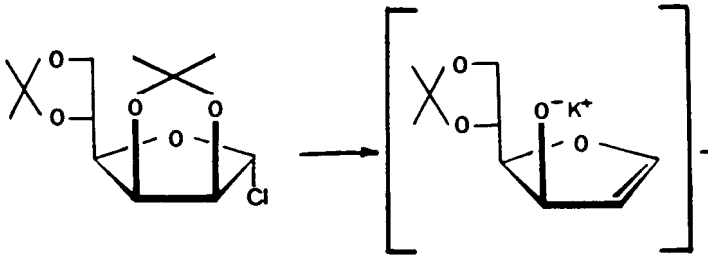
a. Attempted tritylations were unsuccessful.

b. Reaction time with C_8K / reaction time with electrophile.

c. Yield after column chromatography.

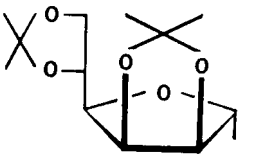
d. Moisture contained in the solvent used for work-up.

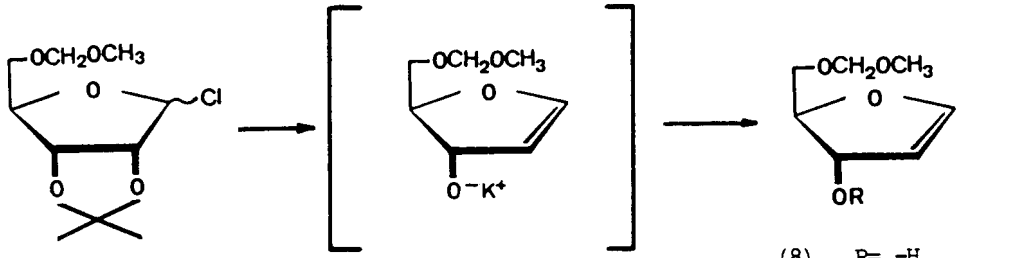
performed on precoated silica gel plates (MERCK 60 F-254) and column chromatography on silica gel (MERCK 230-240 mesh). For ^1H and ^{13}C NMR spectroscopy of the products a BRUKER MSL 300 instrument was used with deuterochloroform (ALDRICH) as solvent and tetramethylsilane as internal standard. Optical rotations were measured in chloroform on a PERKIN ELMER 141 polarimeter.



(1)

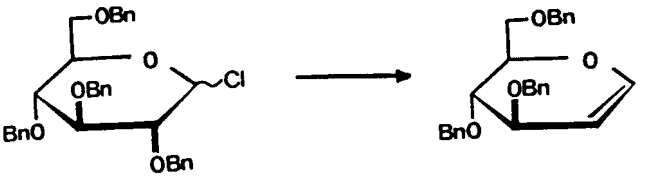
(2) R= -H
(3) R= -Benzyl
(4) R= $-CH_2OCH_3$
(5) R= $-SiMePh_2$

(6) R= 



(7)

(8) R= -H
(9) R= -Benzyl
(10) R= $-CH_2OCH_3$
(11) R= $-SiMePh_2$



(12) (13)

Preparation of Glycals - General Procedure. Potassium (0.6 g, 15.3 mmol) is added in pieces to graphite (1.5 g, 125 mmol) prior degassed for 15 min under argon at 150-160°C. When the potassium melts, the mixture is vigourously stirred by a magnetic stirring bar, thus yielding the bronze-coloured C_8K within 10 min. After cooling and addition of oxolane (25 mL) a solution of 7 mmol of the glycosyl halide[10] in oxolane (20 mL) is quickly added under argon at the respective temperature given in the Table. The reaction mixture almost instantaneously turns black and the glycal is isolated after filtration, evaporation of the solvent, and column chromatography.[20] For alkylations and silylations of the 3-O-unprotected glycals the reductions were performed as above with 5 mmol of the educt by adding 8 mmol of electrophile prior to work-up and stirring the mixture for the respective time given in the Table.

1,4-Anhydro-2-deoxy-5,6-O-isopropylidene-D-*arabino*-hex-1-enitol (2). ^{1}H NMR δ 6.59 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 5.26 (dd, 1H, $J_{1,2} = J_{2,3}$ = 3.1 Hz, H-2), 4.93 (m, 1H, H-3), 4.17 (m, 1H, H-4), 4.51 (d-X-part of an ABX, 1H, $J_{4,5}$ = 7.9 Hz, H-5), 4.02 and 4.18 (d-AB-part of the ABX, 2H, $J_{5,6} = J_{5,6'}$ = 5 Hz, $J_{6,6'}$ = 8.6 Hz, H-6, H-6'), 1.39, 1.47 (s, 6H, CH_3-isopropylidene); ^{13}C NMR δ 150.51 (C-1), 104.16 (C-2), 73.20 (C-3, §), 84.98 (C-4), 73.00 (C-5, §), 67.08 (C-6), 109.40 (=C=), 25.48, 27.20 (CH_3-isopropylidene); oil; $[\alpha]_D^{20}$ -93.6° (c 1.0), lit.:[3] -100° (c 1);

1,4-Anhydro-2-deoxy-3-O-benzyl-5,6-O-isopropylidene--D-*arabino*-hex-1-enitol (3). ^{1}H NMR δ 6.56 (d,1H, $J_{1,2}$ = 2.7 Hz, H-1), 5.23 (dd, 1H, $J_{1,2} = J_{2,3}$ = 2.7 Hz, H-2), 4.60 (dd, 1H, $J_{3,4}$ = 6.9 Hz, H-3), 4.37 (dd, 1H, $J_{4,5}$ = 5.3 Hz, H-4), 4.56 (m, 1H, H-5), 4.08 and 3.97 (d-AB-system, 2H, $J_{6a,6b}$ = 8.5 Hz, $J_{5,6a} = J_{5,6b}$ =6.5 Hz, H-6a, H-6b), 4.48 (AB-system, J_{AB} = 11.7 Hz, -CH_2Ph), 7.28 (bs, 5H, -Ph), 1.36, 1.45 (s, 6H, CH_3-isopropylidene); ^{13}C NMR δ 150.46 (C-1), 101.96 (C-2), 79.55 (C-3), 84.29 (C-4), 73.08 (C-5,§), 66.09 (C-6), 71.03 (-CH_2Ph §), 127.53, 128.31, 129.00 (Ph-), 108.70 (=C=), 25.37, 26.60 (CH_3-isopropylidene); oil; $[\alpha]_D^{20}$ -31.4° (c 1.4), lit.[6] -28° (c 2.4);

§ assignments may be interchanged

1,4-Anhydro-2-deoxy-5,6-O-isopropylidene-3-O-methoxymethyl-D-*arabino*-hex-1-enitol (4). ^{1}H NMR δ 6.55 (d, 1H, $J_{1,2}$ = 2.6 Hz, H-1), 5.20 (dd, 1H, $J_{1,2} = J_{2,3}$ = 2.6 Hz, H-2), 4.72 (dd, 1H, $J_{3,4}$ = 7.0 Hz, H-3), 4.32 (dd, 1H, $J_{4,5}$ = 6.9 Hz, H-4), 4.45 (ddd, 1H, $J_{5,6a} = J_{5,6b}$ = 6.7 Hz, H-5), 3.93 and 4.06 (d-AB-system, 2H, $J_{6a,6b}$ = 8.6 Hz, H-6a, H-6b), 4.60 (AB-system, 2H, $-OCH_2O-$), 3.30 (s, 3H, $-OCH_3$), 1.32, 1.40 (s, 6H, CH_3-isopropylidene); ^{13}C NMR δ 150.50 (c-1), 102.86 (c-2), 77.79 (C-3), 84.11 (C-4), 73.23 (C-5), 66.37 (C-6), 95.64 ($-OCH_2O-$), 55.65 ($-OCH_3$), 109.50 (=C=), 25.51, 26.85 (CH_3-isopropylidene); oil; $[\alpha]_D^{20}$ 13.2° (c 1.0);

1,4-Anhydro-2-deoxy-5,6-O-isopropylidene-3-O-(methyl diphenyl silyl)-D-*arabino*-hex-1-enitol (5). ^{1}H NMR δ 6.49 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1), 4.94 and 4.97 (m, 2H, H-2, H-3), 4.27 (dd, 1H, $J_{3,4} = J_{4,5}$ = 6.2 Hz, H-4), 4.56 (ddd, 1H, $J_{5,6a} = J_{5,6b}$ = 6.2 Hz), 4.05 and 4.11 (d-AB-system, 2H, $J_{6a,6b}$ = 8.5 Hz, H-6a, H-6b), 7.33 and 7.60 (m, 10H, -Ph), 1.36, 1.46 (s, 6H, CH_3-isopropylidene), 0.66 (s, 3H, Me-Si); ^{13}C NMR δ δ 149.88 (C-1), 104.54 (C-2), 73.86 (C-3, §), 84.98 (C-4), 73.23 (C-5, §), 66.32 (C-6), 108.76 (=C=), 25.37, 26.72 (CH_3-isopropylidene), 127.98, 129.70, 134.52, 136.20 (-Ph), -2.25 (CH_3-Si); oil; $[\alpha]_D^{20}$ -59.0° (c 1.6);

(1,3)-(2,3:5,6-Di-O-isopropylidene-α-D-*manno*-furanosyl)-1,4-anhydro-2-deoxy-5,6-O-isopropylidene-D-*arabino*-hex-1-enitol (6). ^{1}H NMR δ 6.57 (d, 1H, $J_{1,2}$ = 2.4 Hz, H-1); 5.17 (s, 1H, H-1'), 5.15 (dd, 1H, $J_{1,2} = J_{2,3}$ = 2.4 Hz, H-2), 4.74 (m, 2H, H-3, H-2'), 4.55 (dd, 1H, $J_{2',3'}$ = 6.1 Hz, H-3'), 4.30 (dd, 1H, $J_{3,4} = J_{4,5}$ = 6.8 Hz, H-4), 4.40 (m, 2H, H-4', H-5), 3.92 - 4.13 (m, 5H, H-5', H-6a, H-6b, H-6a', H-6b'), 1.46 (s, 9H), 1.40 (s, 6H), 1.35 (s, 3H) (CH_3-isopropylidene); ^{13}C NMR δ 150.23 (C-1), 112.57, 109.16, 106.64 (=C=), 103.47 (C-2, §), 103.38 (C-1', §), 85.04, 83.71 (C-4, C-4'), 80.07, 79.60, 78.77 (C-2', C-3, C-3'), 73.49, 72.85 (C-5, C-5'), 66.61, 66.46 (C-6, C-6'), 26.90, 26.72, 25.94, 25.31, 24.59 (CH_3-isopropylidene); m/e (rel.intensity): 428 (M^+, 3); $[\alpha]_D^{20}$ -33.7° (c 3.2), lit.:[11] 13° (c 1)[21]

1,4-Anhydro-2-deoxy-5-O-methoxymethyl-D-*erythro*-pent-1-enitol (8). ^{1}H NMR δ 6.58 (dd, 1H, $J_{1,2}$ = 2.7 Hz, $J_{1,3}$ = 1 Hz, H-1), 5.19 (dd, 1H, $J_{1,2} = J_{2,3}$ =2.7 Hz, H-2), 4.75

(m, 1H, H-3), 4.48 (d-X-part of an ABX system, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 6.2 Hz, $J_{4,5b}$ = 5.5 Hz, H-4), 3.55 and 3.60 (AB-part of the ABX system, 2H, $J_{5a,5b}$ = 10.5 Hz, H-5a, H-5b), 2.65 (bd, 1H, $J_{-OH,3}$ = 7 Hz, -OH), 4.68 (s, 2H, $-OCH_2O-$), 3.38 (s, 3H, $-OCH_3$); ^{13}C NMR δ 150.21 (C-1), 103.45 (C-2), 75.97 (C-3), 87.90 (C-4), 67.92 (C-5), 96.86 ($-OCH_2O-$), 55.39 ($-OCH_3$); oil; $[\alpha]_D^{20}$ 263.8° (c 3.1), lit.:[3] 259° (c 0.91);

1,4-Anhydro-2-deoxy-3-O-benzyl-5-O-methoxymethyl-D-*erythro*-pent-1-enitol (9). ^{1}H NMR δ 6.59 (dd, 1H, $J_{1,2}$ = 2.5 Hz, $J_{1,3}$ = 0.4 Hz, H-1), 5.18 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 2.5 Hz, H-2), 4.64 (m, 2H, H-3, H-4), 3.54 and 3.58 (AB-part of an ABX system, 2H, $J_{4,5a}$ = 6.5 Hz, $J_{4,5b}$ = 4.9 Hz, $J_{5a,5b}$ = 10.8 Hz, H-5a, H-5b), 4.54 (s, 2H, $-OCH_2O-$), 3.36 (s, 3H, $-OCH_3$), 4.65 (2H, $-CH_2Ph$), 7.20-7.50 (m, 5H, -Ph); ^{13}C NMR δ 153.11 (C-1), 100.76 (C-2), 82.65 (C-3), 85.10 (C-4), 67.84 (C-5, §), 96.88 ($-OCH_2O-$), 55.62 ($-OCH_3$), 69.82 ($-CH_2Ph$, §), 127.86, 128.11, 128.51, 129.31 (-Ph); oil; $[\alpha]_D^{20}$ 119.4° (c 3.0), lit.:[6] 116° (c 1.7);

1,4-Anhydro-2-deoxy-3,5-di-O-methoxymethyl-D-*erythro*-pent-1-enitol (10). ^{1}H NMR δ 6.56 (d, 1H, $J_{1,2}$ = 2.6 Hz, H-1), 5.14 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 2.6 Hz, H-2), 4.84 (dd and X-part of an ABX system, 2H, $J_{3,4}$ = 3 Hz, $J_{4,5a}$ =6.1 Hz, $J_{4,5b}$ =5.3 Hz, H-3, H-4), 3.59 and 3.62 (AB-part of an ABX system, 2H, $J_{5a,5b}$ = 10.6 Hz, H-5a, H-5b), 4.64, 4.69 (s, 4H, $-OCH_2O-$), 3.38 (s, 6H, $-OCH_3$); ^{13}C NMR δ 150.29 (C-1), 101.18 (C-2), 81.83 (C-3), 85.66 (C-4), 67.60 (C-5), 96.84, 95.45 ($-OCH_2O-$), 55.41 ($-OCH_3$); oil; $[\alpha]_D^{20}$ 157.6° (c 3.4);

1,4-Anhydro-2-deoxy-5-O-methoxymethyl-3-O-(methyl diphenyl silyl)-D-*erythro*-pent-1-enitol (11). ^{1}H NMR δ 6.44 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.95 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 3.0 Hz, H-2), 4.91 (dd, 1H, $J_{3,4}$ = 3 Hz, H-3), 4.53 (X-part of an ABX system, 1H, $J_{4,5a}$ = 6.5 Hz, $J_{4,5b}$ = 4.8 Hz, H-4), 3.33 and 3.36 (AB-part of the ABX system, 1H, $J_{5a,5b}$ = 10.7 Hz, H-5a, H-5b), 4.49 (s, 2H, $-OCH_2O-$), 3.21 (s, 3H, $-OCH_3$), 7.34, 7.59 (m, 10H, -Ph), 0.67 (s, 3H, CH_3-Si); ^{13}C NMR δ 149.48 (C-1), 105.21 (C-2), 77.00 (C-3), 87.56 (C-4), 67.31 (C-5), 96.58 ($-OCH_2O-$), 125.37, 127.96, 128.29, 129.06, 129.71, 134.40 (-Ph), 4.50 (CH_3-Si); oil; $[\alpha]_D^{20}$ 43.9° (c 0.6);

1,5-Anhydro-3,4,6-tri-O-benzyl-D-*arabino*-hex-1-enitol (13). ^{1}H NMR δ 6.32 (dd, 1H, $J_{1,2}$ = 6.2 Hz, $J_{1,3}$ = 0.3 Hz, H-1), 4.73 - 4.85 (m, 2H, H-2, H-4), 4.18 (dd, 1H, $J_{2,3}$ = 3 Hz, H-3), 4.02 (m, 1H, H-5), 3.71 - 3.90 (m, 2H, H-6a, H-6b), 7.20 (m, 15H, -Ph), 4.47 - 6.64 (m, 6H, $-CH_2Ph$); ^{13}C NMR δ 144.33 (C-1), 99.62 (C-2), 76.52, 75.43, 74.17, 73.26, 73.10, 70.02 (C-3, C-4, C-5, $-CH_2Ph$), 66.28 (C-6), 127.31, 127.45, 127.57, 127.71, 128.12, 137.81, 138.02, 138.15 (-Ph); mp 56-57 °C, lit.:[19] 55 °C, $[\alpha]_D^{20}$ -3.0° (c 4), lit.:[19] -2.7° (c 16.5);

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