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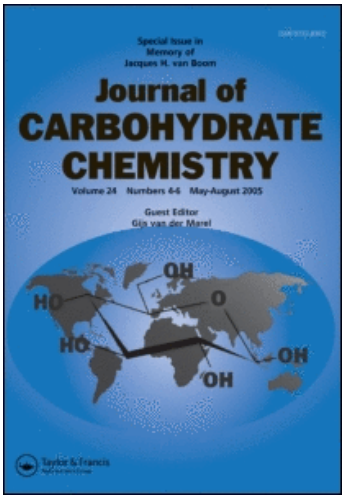

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REFORMATSKY-TYPE BRANCHING OF ALDONOLACTONES[1]

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ABSTRACT

Condensation of furanoid as well as pyranoid aldonolactones with organozinc reagents obtained from different haloalkanoates and the zinc/silver-graphite surface compound gave in high yield carbon chain extended 3- or 4-ulofuranos- (or -pyranos)onates.

INTRODUCTION

The discovery of *C*-nucleosides and their biological properties[2,3] initiated the search for the synthesis of *C*-glycosyl compounds. Aldonolactones are often commercially available or readily obtained from the corresponding sugars but only a few reports of the use of aldonolactones for the synthesis of *C*-glycosyl compounds have been published so far.[4-8] It seems noteworthy that although preliminary reports described the *Reformatsky*-type reaction of 2,3:5,6-di-*O*-cyclohexylidene-**D**-*mannono*-1,4-

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lactone,[9,10] this convenient method for carbon chain extension at the anomeric centre has up to now found only one application in the carbohydrate field.[11] This might be due to the fact that the rather limited set of conditions resulted in only moderate yields. Recently, improvements have been achieved by the use of a zinc/silver couple dispersed on the surface of graphite.[12] This zinc/silver-graphite surface compound, obtained from the reaction of equimolar amounts of C_8K and $ZnCl_2$/AgOAc (0.1 molar ratio) was shown to be of unprecedented high reactivity and thus enabled *Reformatsky* reactions to be performed under very mild conditions.

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RESULTS AND DISCUSSION

Treatment of aldono-1,4-lactones **1** or **2** and -1,5-lactones **3** or **4** with a *Reformatsky* reagent prepared from α-haloesters **6, 7, 9, 10** or alkyl 2-(bromomethyl)-acrylates **8** or **11** and the zinc/silver-graphite compound resulted in the formation of the corresponding 3- or 4-ulofuranos (or -pyranos)onates **12-20** in good yield. These reactions were usually performed by adding a solution of the corresponding haloester and the lactone in dry tetrahydrofuran to a suspension of the Zn/Ag-graphite surface compound in the same solvent at -40 °C under vigorous stirring. Normally, the reactions were completed within 20 min at -40 °C and additional 30 min at 0 °C. Due to their reactivity the *Reformatsky* reagents can be applied only in small excess, whereas under "classical" conditions usually a 2-3 fold excess of the reagent had to be applied.[9-12] Significant improvements of the yields were achieved.

The NMR spectra supported the assigned structures. The one-proton peak at δ=4.7-4.9 for **12, 13, 15,** and **17** (and δ=3.54 for **16,** δ=5.73 for **18**) was exchangeable with D_2O and thus assigned to the anomeric hydroxyl group. The anomeric configuration has been assigned through the multiplicity of the adjacent CH_2-protons in the ^{1}H-NMR spectra which has been used as a

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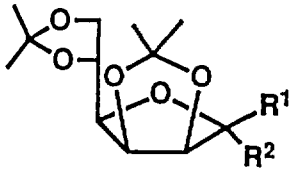
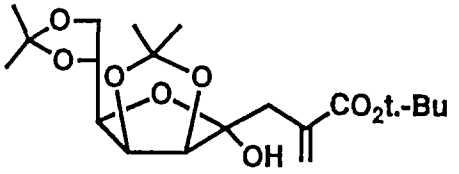


1 R^1, R^2= O
12 R^1= CH_2CO_2Et, R^2= OH



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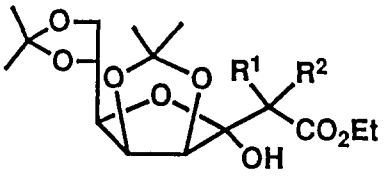
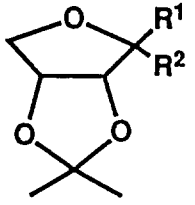
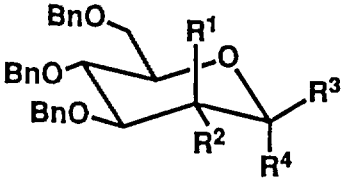


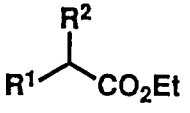
14 R^1, R^2= F, H
15 R^1= Br, R^2= H
16 R^1= H, R^2= Br



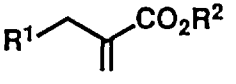
2 R^1, R^2= O
17 R^1= OH, R^2= CH_2CO_2Et
18 R^1= OH, R^2= $CH_2C(=CH_2)CO_2Et$



3 R^1= H, R^2= OBn, R^3, R^4= O
4 R^1= OBn, R^2= H, R^3, R^4= O
19 R^1= H, R^2= OBn, R^3= CH_2CO_2Et, R^4= OH
20 R^1= OBn, R^2= H, R^3= CH_2CO_2Et, R^4= OH



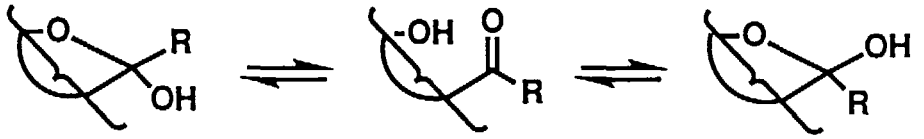
6 R^1= Br, R^2= H
7 R^1= Cl, R^2= H
9 R^1= Br, R^2= F
10 R^1= Br, R^2= Br



8 R^1= Br, R^2= $C(CH_3)_3$
11 R^1= Br, R^2= Et

criterion.[11,13] Although the given assignments for our products are in perfect accordance with this empirical criterion, its general applicability must be questioned since no direct and independent assignment of the configuration at the anomeric centre was made for these compounds. Consequently, we performed semi-empirical MO-calculations for purposes of assigning anomeric configurations of our products.[14]

It may be assumed as depicted in the Figure that for each of the products both possible anomers **A** and **C** might be in equilibrium *via* their open chain form **B**:[15]



A **B** **C**

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To estimate this equilibrium AM1 calculations were performed and the calculated values for the heat of formation of the respective anomers were compared. These calculations revealed for all products significant differences (3-7 Kcal/mol) in the heat of formation of the respective **A/C** couples, hence clearly indicating the preferred anomer. By comparison of the NMR-spectra and these AM1 calculations it seems reasonable that the assigned[9,10] stereochemistry for ethyl 2-deoxy-4,5:7,8-di-*O*-cyclohexylidene-α-**D**-*manno*-3,6-furanoso-3-octulosonate has to be reversed.

As shown for the synthesis of **12**, yields drop only slightly using the less reactive ethyl chloroacetate (**7**) instead of ethyl bromoacetate (**6**). Contrary to findings with carbohydrate uloses[17] no glycidate formation occurred on the reaction of lactone **1** with the α-bromozinc ester enolate from ethyl dibromo-acetate (**10**). The two diastereomeric 2-deoxy-2-bromo-3,6-furanoso-3-

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Table: ^{1}H-NMR Spectral Data

H (δ)	12	15	16	17	13	18
H-2	2.72	4.38	4.56	2.76		
H-2′	2.82			2.86		
H-3					2.90	2.77
H-3′					2.73	2.94
H-4	4.51	4.61	4.74	4.44		
H-5	4.84	4.85	4.93	4.83	4.43	4.33
H-6	4.09	4.18	4.13	4.02	4.83	4.80
H-6′				3.92		
H-7	4.35	4.35	4.37		4.01	3.95
H-7′						3.82
H-8	3.99	4.03	4.04		4.34	
H-8′	4.06	3.94	4.09			
H-9					4.06	
H-9′					3.98	
Me	1.29	1.35	1.29	1.29	1.32	1.28
Me	1.37	1.36	1.38	1.45	1.37	1.45
Me	1.42	1.41	1.44		1.42	
Me	1.46	1.50	1.46		1.49	
Me of ester	1.29	1.32	1.30	1.27	1.50	1.27
CH_2 of ester	4.20	4.27/ 4.30	4.27	4.19		4.20
OH	4.89	4.80	3.54	4.79	4.71	5.83
$=CH_A$					5.76	5.83
$=CH_B$					6.19	6.28

J (Hz)	12	15	16	17	13	18
2,2′	16.6			16.7		
3,3′					14.1	14.2
4,5	5.8	5.8	5.8	5.9		
5,6	3.7	3.8	3.6	3.7	5.9	5.9
5,6′				0.0		
6,6′				10.3		
6,7	8.0	7.7	8.0		3.9	4.0
6,7′						0.0
7,7′						10.2
7,8	6.1	6.2	4.4		6.3	
7,8′	4.5	4.5	5.9			
8,8′	8.7	8.7	8.8			
8,9					7.8	
8,9′					4.8	
9,9′					8.6	
ester	7.2	7.1 13.9	7.1	7.2		7.1
H_A-H_B					1.8	1.3

octulosonates (**15**) and (**16**) were easily separated by chromatography as opposed to the corresponding 2-fluoro analogs **14**. The absolute configuration at position C-2 could not be assigned for these compounds.

EXPERIMENTAL

General procedures. Melting points are uncorrected (*Tottoli*), optical rotations were obtained using a Perkin-Elmer 141 polarimeter, NMR spectra for solutions in $CDCl_3$ (internal Me_4Si) were recorded using Bruker AM-250, and AM-400 instruments, IR spectra (3% solution in $CHCl_3$) on a Perkin-Elmer 298. TLC was performed on silica gel (Merck, 5554, detection by spraying with a 5 % solution of vanillin in concd sulfuric acid followed by heating at 150 °C). MS spectra were recorded using a Varian-112S instrument.

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General Procedure for Reformatsky-type Reactions. Graphite (Fluka, 0.78 g, 65 mmol) and clean potassium (0.33 g, 8.44 mmol) were stirred at 150 °C under argon as previously described.[18] To the resulting bronze-coloured C_8K suspended in dry tetrahydrofuran (20 mL) a mixture of anhydrous zinc chloride (0.55 g, 4.1 mmol) and silver acetate (0.06 g, 0.36 mmol) was added in several portions at room temperature with vigorous stirring. The addition of these salts caused the solvent to boil. Refluxing was continued for an additional 20 min, the suspension was cooled to -40 °C and a solution of 3.3 mmol of the corresponding lactone and 4.3 mmol of halo ester in abs tetrahydrofuran (5 mL) was slowly added. After stirring at this temp for 20 min the mixture was allowed to warm to 0 °C, stirred further for 30 min, filtered over a pad of celite, diluted with ethyl acetate (50 mL), and extracted with ice water (5 mL) and brine (5 mL). The organic layer was dried over sodium sulfate, the solvents were evaporated below 35 °C and the remaining residue subjected to column chromatography (ethyl acetate/hexane 1:5 (*v/v*)) to afford the corresponding products.

Ethyl 2-Deoxy-4,5:7,8-di-O-isopropylidene-α-D-manno-3,6-furanoso-3-octulosonate (12). From **1** and **6** 1.03 g (90%) or from **1** and **7** 0.97 g (85 %) as an oil : $[\alpha]_D^{25}$ 5.6° (*c* 2.7, chloroform); IR 3460 (OH) and 1715 (ester) cm^{-1}; ^{13}C-NMR ($CDCl_3$) δ 14.01 (CH_3, ester), 24.44, 25.31, 25.86, 26.83 (CH_3, isopropylidene), 38.31 (CH_2), 61.03 (CH_2), 66.87 (CH_2), 73.02, 79.36, 80.14, 85.65 (CH), 103.89, 109.13, 112.82 ($C_{quat.}$), 172.04 (COO); MS (c.i., isobutane) 329 ($M-H_2O+1$).

Anal. Calcd for $C_{16}H_{26}O_8$: C, 55.48; H, 7.57. Found: C, 55.61; H, 7.39.

Tert-butyl 2,3-Dideoxy-2-C-methylene-5,6:8,9-di-O-isopropylidene-α-D-manno-4,7-furanoso-4-nonulosonate (13). From **1** and **8** 1.2 g (91 %): mp 62-64 °C, $[\alpha]_D^{25}$ 7.5° (*c* 1.6, chloroform); IR 3420 (OH) and 1710 (ester) and 1630 cm^{-1} (C=C); ^{13}C-NMR ($CDCl_3$) δ 24.56, 25.28, 25.91, 26.74 (CH_3, isopropylidene), 27.86 ($(CH_3)_3$, ester), 36.39, 66.73 (CH_2), 73.18, 78.62, 80.21 (CH), 81.53 ($C_{quat.}$), 84.95 (CH), 105.01, 108.87, 112.45 ($C_{quat.}$), 128.72 ($=CH_2$), 136.33 ($C_{quat.}$), 168.61 (COO); MS (c.i., isobutane) 383 ($M-H_2O+1$).

Anal. Calcd for $C_{20}H_{32}O_8$: C, 59.99 H, 8.05. Found: C, 60.20; H, 7.91.

Ethyl 2-Deoxy-2-fluoro-4,5:7,8-di-O-isopropylidene-α-D-manno-3,6-furanoso-3-octulosonate (14). From **1** and **14** 1.01 g (84%) were obtained as a 1:1 mixture of diastereomers, inseparable by chromatography: IR 3835 (OH) and 1725 cm^{-1} (ester); ^{13}C-NMR ($CDCl_3$) δ 88.76 (d, $J_{C,F}$ =191.8 Hz, C-2),103.58 (d, $J_{C,F}$ =17.6 Hz, C-3), 166.39 (d, $J_{C,F}$= 23.0 Hz, COO), MS (c.i., isobutane) 365 (M+1), 347 ($M-H_2O+1$).

(2 RS) Ethyl 2-Deoxy-2-bromo-4,5:7,8-di-O-isopropylidene-α-D-manno-3,6-furanoso-3-octulosonate (15) and **(2 SR) Ethyl 2-Deoxy-2-bromo-4,5:7,8-di-O-isopropylidene-α-D-manno-3,6-furanoso-3-octulosonate (16).** According to the general procedure 1.0 g

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(71 %) of **15** and 0.25 (18 %) of **16** could be obtained. Data for the **15** (faster moving on TLC): oil, $[\alpha]_D^{25}$ 46.6° (*c* 1.6, chloroform); IR 3840 (OH) and 1725 cm^{-1} (ester); ^{13}C-NMR ($CDCl_3$) δ 13.74 (CH_3, ester), 24.26, 25.30, 25.77, 26.74 (CH_3, isopropylidene), 40.94 (CH), 62.49, 66.57 (CH_2), 72.86, 79.79, 80.72, 84.46 (CH), 104.93, 109.17, 112.29 ($C_{quat.}$), 169.87 (COO); MS (c.i., isobutane) 426 (20 %) and 428 (19%) (M+1).

Anal. Calcd for $C_{16}H_{25}BrO_8$: C, 45.19; H, 5.93. Found: C, 45.27; H, 5.78.

Data for **16**: oil, $[\alpha]_D^{25}$ -16.4° (*c* 0.6, chloroform); IR 3840 (OH) and 1740 cm^{-1} (ester); ^{13}C-NMR ($CDCl_3$) δ 13.76 (CH_3, ester), 24.42, 25.36, 25.81, 26.90 (CH_3, isopropylidene), 48.59 (CH), 62.16, 66.83 (CH_2), 72.84, 79.52, 80.63, 85.70 (CH), 94.17, 102.99, 109.32 ($C_{quat.}$), 168.31 (COO); MS (c.i., isobutane) 426 and 428 (M+1).

Anal. Calcd for $C_{16}H_{25}BrO_8$: C, 45.19; H, 5.93. Found: C, 45.25; H, 6.00.

Ethyl 2-Deoxy-4,5-O-isopropylidene-β-D-erythro-3,6-furanoso-3-hexulosonate (17). According to the general procedure from **2** and **6** 0.72 g (88 %) **17** could be obtained as an oil: $[\alpha]_D^{25}$ -55.9° (*c* 4.1, chloroform); IR 3460 (OH) and 1720 cm^{-1} (ester); ^{13}C-NMR ($CDCl_3$) δ 13.79 (CH_3, ester), 24.58, 25.99 (CH_3, isopropylidene), 38.24, 60.77, 70.98 (CH_2) 80.33, 84.98 (CH), 104.35, 112.24 ($C_{quat.}$), 171.89 (COO); MS (c.i., isobutane) 229 ($M-H_2O+1$).

Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.41; H, 7.47.

Ethyl 2,3-Dideoxy-5,6-O-isopropylidene-2-C-methylene-β-D-erythro-4,7-furanoso-4-heptulosonate (18). From **2** and **8** 0.83 g (92 %) **18** could be obtained as an oil: $[\alpha]_D^{25}$ -41.8° (*c* 0.6, chloroform); IR 3440

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(OH), 1710 (ester) and 1630 cm^{-1} (C=C); ^{13}C-NMR ($CDCl_3$) δ 13.90 (CH_3, ester), 24.96, 26.26 (CH_3, isopropylidene), 36.59, 61.28, 70.76 (CH_2), 80.54, 84.45 (CH), 105.66, 112.19 ($C_{quat.}$), 129.66 (=CH_2), 135.07 ($C_{quat.}$), 169.22 (COO); MS (c.i., isobutane) 255 (M-H_2O+1).

Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.29; H, 7.44.

Ethyl 2-Deoxy-4,5,6,8-tetra-O-benzyl-α-D-gluco-3,7-pyranoso-3-octulosonate (19). From **3** and **6** 1.92 g (89%) **19** could be obtained as an oil: $[\alpha]_D^{25}$ -5.3° (*c* 1.3, chloroform); IR 3460 (OH) and 1710 cm^{-1} (ester); ^{1}H-NMR ($CDCl_3$) δ 1.24 (t, 3H, J= 7.1 Hz, CH_3), 1.61 (bs, 1H, OH), 2.33 and 2.77 (AB, J= 15.5 Hz, CH_2), 3.33 (dd, 1H, J= 1.5, 9.5 Hz), 3.6-3.8 (m, 3H), 4.03 (ddd, J = 1.8, 3.6, 10.0 Hz, 1H), 4.1-4.25 (qxAB, J= 12, 7.1 Hz, CH_2-ester) 4.5-4.7 (m, 4H), 4.85 (d, J= 10.9 Hz, 1H), 4.95 (s, 2H), 4.98 (d, J= 11.5 Hz, 1H), 5.36 (d, J=1.4 Hz, 1H), 7.15-7.40 (m, 20 H, aromat); ^{13}C-NMR ($CDCl_3$) δ 13.98 (CH_3, ester), 40.50, 60.96, 68.55 (CH_2), 71.43 (CH), 73.23, 74.79, 75.15, 75.54 (CH_2, benzyl), 78.46, 81.91, 83.11 (CH), 97.06 (C-$3_{quat.}$), 127.46, 127.54, 127.64, 126.67, 127.73, 127.84, 127.98, 128.05, 128.21, 128.27, 128.33 (CH, aromat), 137.80, 138.21, 138.25, 138.51($C_{quat.}$), 172.27 (COO); MS (c.i., isobutane) 609 (M-H_2O+1).

Anal. Calcd for $C_{38}H_{42}O_8$: C, 72.82; H, 6.75. Found: C, 72.95; H, 6.81.

Ethyl 2-Deoxy-4,5,6,8-tetra-O-benzyl-α-D-manno-3,7-pyranoso-3-octulosonate (20). From **4** and **6** 1.83 g (85 %) of **20** could be obtained as an oil: $[\alpha]_D^{25}$ 8.7° (*c* 4.1, chloroform); IR 3440 (OH) and 1710 cm^{-1} (ester); ^{1}H-NMR ($CDCl_3$) δ 1.25 (t, J= 7.1 Hz, CH_3), 1.65 (bs, 1H, OH), 2.35 and 3.02 (AB, J= 15.6 Hz, CH_2), 3.65-4.22 (m, 7H), 4.52 (d, J= 12 Hz, 1H), 4.59 (d, J=11 Hz, 1H), 4.65 (d, J=12 Hz, 1H), 4.66 (d, J=11.6 Hz, 1H), 4.79 (s, 2H), 4.88 (d, J=11 Hz, 1H), 5.03 (d, J=11.5 Hz, 1H), 5.27 (s, 1H), 7.2-7.45 (m, 20H); ^{13}C-NMR ($CDCl_3$) δ 13.91 (CH_3, ester), 40.00, 60.91, 69.19 (CH_2),

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72.99 (CH), 73.18, 74.37, 74.86 (CH_2, benzyl), 74.91, 77.51, 81.31 (CH), 97.35 ($C_{quat.}$), 127.14, 127.26, 127.47, 127.53, 127.70, 127.85, 128.05, 128.13, 128.19, 128.33, 128.58, 128.65, 128.82 (CH, aromat), 138.30, 138.52, 138.63 ($C_{quat.}$), 172.52 (COO); MS (c.i., isobutane) 609 ($M-H_2O+1$).

Anal. Calcd for $C_{38}H_{42}O_8$: C, 72.82; H, 6.75. Found: C, 73.04; H, 6.66.

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15. As a consequence of this equilibrium a "ketonic decarboxylation" has been reported for sodium 2-deoxy-4,5:7,8-di-*O*-cyclohexylidene-α-**D**-*manno*-3,6-furanoso-3-octulosonate (ref. 9, 10).

16. The lowest difference in energy was found for **17** and **18**. ^{1}H-NMR spectroscopic investigation of concentrated solutions of **17** or **18** showed the presence of the respective α-anomer in about 3-5%. This is in excellent agreement with the calculations.

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