Oxidation of Fully Protected Glycals by Hypervalent Iodine Reagents

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A new application of organoiodine(III) is presented. Fully protected glycals are directly converted into 2,3-dihydro-4*H*-pyran-4-ones by [hydroxy(tosyloxy)iodo]benzene (PhI(OH)OTs, **1**). The detailed study reveals that this conversion is independent of the relative stereochemistry as well as the nature of protection on the pyran ring. 3-*O*-Silyl groups are most smoothly converted into the keto group giving 2,3-dihydro-4*H*-pyran-4-ones in yields up to 74%. In contrast, 4,6-di-*O*-acetyl-3-deoxyglucal (**19**) affords the rearranged oxidation product **32**. Both observations can be reconciled by the proposed mechanism.

Introduction

Over the last 15 years, polycoordinated iodine compounds in the oxidation states III and V have emerged as new synthetic tools in organic chemistry with unusual properties as described in recent reviews.[1] A major application for iodine(V) was the development of a useful new reagent for the oxidation of alcohols by Dess and Martin.[2] Important synthetic contributions in the chemistry of iodine in oxidation state III include α-oxidation of ketones and silyl enol ethers[3] and *syn*-1,2 ditosyloxylation of olefinic double bonds with [hydroxy(tosyloxy)iodo]benzene,[4] the Koser reagent. Despite the large number of recent publications describing uses of organoiodine(III), very few examples for multifunctional substrates such as carbohydrates can be found.[5]

Recently, we briefly reported our findings on the unprecedented direct formation of 2,3-dihydro-4*H*-pyran-4-ones from O-3-protected glycals in the presence of PhI(OH)OTs (**1**).[6] There are various methods for the preparation of 2,3-dihydro-4*H*-pyran-4-ones[7] involving *de novo* synthesis by cycloaddition,[8] enantioselective Mukaiyama-aldol reactions,[9] or allylic oxidation of glycals with various reagents.[10,11] The latter approach, however, requires unprotected glycals as starting material affording the corresponding unprotected 2,3-dihydro-4*H*-pyran-4-ones; further manipulations on their remaining hydroxy groups, in particular alkylation,[12f] are limited to mild conditions. Due to these synthetic limitations, these dihydropyranones comprise a relatively unexplored class of highly functionalized chiral building blocks.[12] We now report an extension of our new method, particularly the development of simple routes to fully hydroxy differentiated 2,3-dihydro-4*H*-pyran-4-ones.

Results

Preliminary experiments were performed to determine the range of protecting groups on O-3 compatible with this oxidation process. Thus, a set of glucals **2a–f** was synthesized that differed at O-3 (Scheme 1). These glucals were chosen because they are easily prepared[13] by enzymatic regioselective deacetylation of commercially available tri-*O*-acetyl-D-glucal (**2a**) followed by appropriate protection of the allylic hydroxy group. Upon treatment with **1**, all of these afforded dihydropyranone **3** in varying yields. Thus, the ketone functionality can be elaborated from diverse precursors including alcohols, esters, acetals, and ethers in a regiospecific process. The organoiodine(III)-mediated oxidation turned out to be

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Scheme 1

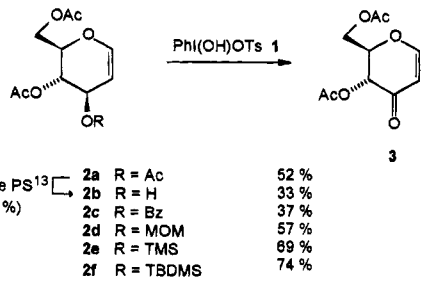
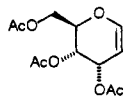
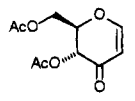
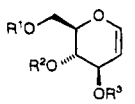
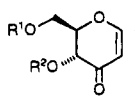
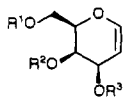
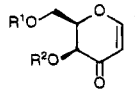
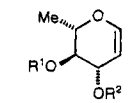
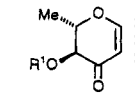
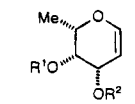
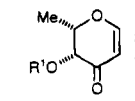
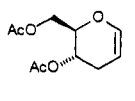
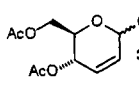


Table 1. [Hydroxy(tosyloxy)iodo]benzene-Promoted Oxidations of Glycals

entry	glycal		2,3-dihydro-4*H*-pyranone		% isolated yield[a]
1		**4**		**3**	45
2		**5** $R^1=R^2=R^3=$ Bn		**20**	49[b]
3		**6** $R^1=R^3=$ Ac; $R^2=$ H		**21**	32
4		**7** $R^1=R^3=$ Ac; $R^2=CH_2OCH_3$		**22**	48
5		**8** $R^1=R^3=$ Ac; $R^2=SiMe_2{}^tBu$		**23**	41
6		**9** $R^1=$ Ac; R^2-$R^3=SnBu_2$		**21**[d]	42
7		**10** $R^1=R^2=R^3=$ Ac		**24**[c]	58
8		**11** $R^1=R^2=R^3=$ Bn		**25**	57[b]
9		**12** $R^1=SiMe_2{}^tBu$; $R^2=R^3=$ Ac		**26**	43
10		**13** $R^1=R^3=SiMe_2{}^tBu$; $R^2=$ Ac		**26**	72
11		**14** $R^1=R^2=$ Ac		**27**[c]	48
12		**15** $R^1=R^2=$ Bn		**28**	53[b]
13		**16** $R^1=R^2=SiMe_2{}^tBu$		**29**	67
14		**17** $R^1=R^2=$ Ac		**30**	50
15		**18** $R^1=R^2=$ Bn		**31**	58[b]
16		**19**		**32**	31[e]

[a] Isolated yields after rapid workup and flash chromatography. [b] 1-*O*-Benzylated 2-deoxy-3-uloses are formed as byproducts in cases where the reaction is carried out in more concentrated solutions. [c] Reference 10. [d] R^2 = H. [e] Reference 27.

particularly efficient for 3-O-silylated derivatives **2e** and **2f**. The lower yield for glucal **2b** can be ascribed to competing direct nucleophilic attack of the hydroxy group on the electron-deficient iodine.

In addition, the process is independent of the relative stereochemistry of the alcohol starting material as well as insensitive to the nature and number of protecting groups on the remaining stereocenters, as shown in Table 1. Thus, per-O-benzylated glycals (entries 2, 8, 12, and 15) and the per-O-silylated rhamnal **16** (entry 13) reacted in an analogous manner, affording **20**, **25**, **28**, **29** and **31** which were unknown or for which no general access was previously available.[14] Additionally we found that *in situ* generation of Koser's reagent by slow addition of anhydrous *p*-toluenesulfonic acid to a mixture of (diacetoxyiodo)benzene ($PhI(OAc)_2$) and peracetylated or perbenzylated glycal in acetonitrile gives 2,3-dihydro-4*H*-pyran-4-ones in slightly better yields. The use of powdered molecular sieves (3 Å) is essential. Other hypervalent iodine reagents like $PhI(O_2CCH_3)_2$, $PhI(O_2CCF_3)_2$, and $PhI(OCH_3)OTs$[15] were ineffective oxidants, giving yields of 0–10%, as did borontrifluoride–diethyl ether- or trimethyloxonium tetrafluoroborate-activated iodosylbenzene. In contrast to these results, 3-deoxyglucal **19** was oxidized by Koser's reagent with rearrangement of the olefinic double bond, affording unsaturated hexose **32** as the major product (entry 16).[16]

It may be noted that alternatively per-O-acetylated derivatives **24** (40%) and in particular **3** (95%) and **27** (94%) may be prepared by palladium (II)- or by PDC-promoted oxidations of the corresponding glycals followed by acetylation as described by Czernecki *et al.*[10a,11b]

Chemical manipulations in the carbohydrate field are often governed by the feasibility of differential protection. Therefore, we applied our method in the synthesis of hydroxy differentiated *erythro*- and *threo*- 2,3-dihydro-4*H*-pyran-4-ones **21**–**23** and **26** in a short and efficient manner (Table 1). The former were conveniently obtained by regioselective, unidirectional transesterification of D-glucal (entry 2 with $R^1 = R^2 = R^3 =$ H) using vinyl acetate and lipase PS,[13] followed by protection of the 4-hydroxy group affording **6**–**8** and subsequent allylic oxidation with Koser's reagent (entries 3–5). Due to the lability of partially protected 2,3-dihydro-4*H*-pyran-4-one **21**, the isolated yield was substantially lower than was estimated from the crude ^{1}H NMR spectrum. Alternatively, **21** was synthesized either by regioselective deacetylation of **3** at pH 7 with lipase CC (23%) or by iodine(III) oxidation of the *O*,*O*′-dibutylstannylene acetal **9** (42%) (entry 6).[17] In contrast, differential protection of the *threo*-series was directly achieved by regioselective silylation of D-galactal (entry 7 with $R^1 = R^2 = R^3 =$ H) with TBDMS chloride in the presence of imidazole. Depending on the number of molar equivalents of the silylating reagent employed, either the mono- or bissilylated glycals **12** or **13**, respectively, were obtained after acetylation, both of which gave **26** when oxidized in the presence of PhI(OH)OTs (entries 9 and 10). Again, in terms of yield the 3-siloxy group turned out to be superior to the 3-acetoxy group.

Discussion

The results described above show that organoiodine (III)-promoted oxidation of fully protected glycals is an efficient and general new route to 2,3-dihydro-4*H*-pyran-4-ones. Additionally, a careful search for byproducts was conducted in order to gain mechanistic insights into this reaction. For example, when **2a** was exposed to **1** apart from desired dihydropyranone **3**, an inseparable mixture of **33a** and **33b** in up to 5% yield was isolated. Yields for **33a,b** could be raised slightly when the reaction was performed in the presence of a 4-fold excess of tetra-*n*-

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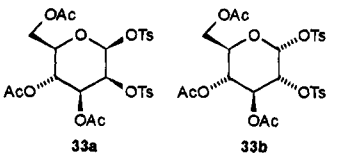
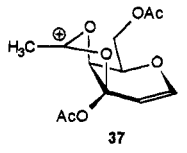
(15) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988.
(16) For the reaction of 2,3-dihydropyran with **1** see: Schaumann, E.; Kirschning, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1481.
(17) **10** is readily available by irreversible transesterification using vinyl acetate and lipase OF which afforded 6-*O*-acetyl-D-glucal[13] followed by Bu_2SnO-promoted stannylation in refluxing toluene.



butylammonium tosylate (Bu_4NOTs). The anomeric protons of the so far unknown *vic*-bis(tosyloxy)pyrans **33a** and **33b** are significantly shifted downfield (close to 6 ppm) in the ^1H NMR spectrum compared to anomeric protons in unprotected aldoses. The ditosylates turned out to be very labile compounds, as proposed before.[4b] A mechanism which is consistent with all observations is outlined in Scheme 2. The sequence is initiated by electrophilic attack of the hypervalent iodine on the enol ether moiety, giving an oxonium ion **34**. Reductive elimination of PhI and H_2O leads to carboxonium ion **35**, which, in the case of **35a** (X = OR) generates the ketone functionality upon rupture of the O–R bond of the protective group.[18] The less stable this bond is in the presence of a neighboring cation, as for the cases of the 3-*O*-silyl ethers **2e**, **2f**, **13**, and **16**, the more facile this process becomes. In contrast, oxonium ion **35b** (X = H) cannot undergo fragmentation as described for **35a**. Instead, it is trapped by hydroxide ion from Koser's reagent **1** as found for the oxidation of **19** (Table 1, entry 16). It should be pointed out that oxonium ion **35b** is identical with the intermediate postulated for the Ferrier rearrangement.[19] Regioselective trapping of cations α to the ring oxygen by hard nucleophiles is commonly observed in these rearrangements, which is in accordance with our observations. Formation of the byproducts **33a,b** is apparently due to trapping of the intermediates **34** and **36** by the nucleophilic tosyloxy ligands which are also present in the reaction mixture.

This mechanistic proposal is further supported by the following observations. The oxidation proceeds considerably more cleanly for tri-*O*-acetyl-D-galactal (**10**) than for the corresponding glucal **2a**. This is readily rationalized on the basis that the axial acetyl group in **10** provides additional anchimeric stabilization of the intermediate oxonium ion, as depicted in **37**. Apart from having

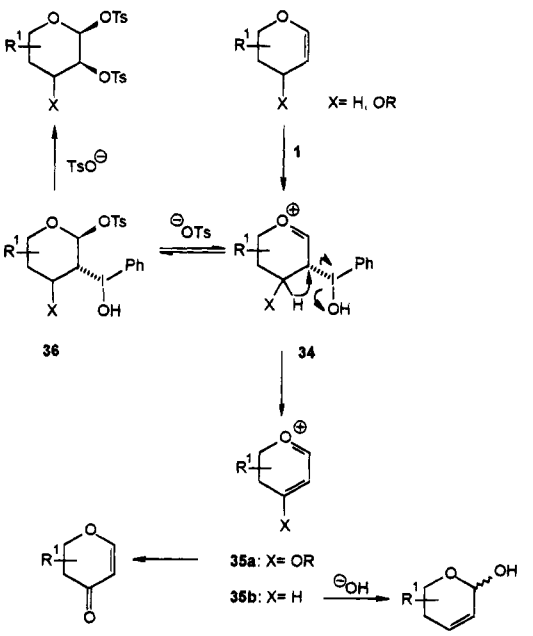


mechanistic resemblances with the Ferrier rearrangement (*vide supra*) this process shows similarities to the palladium(II)-catalyzed dehydrosilylation of silyl enol ethers[20] as well as to their β-functionalization by a combination of iodosylbenzene and trimethylsil azide.[21]

Conclusions

Oxidation of fully protected glycals of the type described in this paper appears to be very general compared to existing methods and can be utilized in the presence of a variety of reactive protective groups. Moreover, the approach avoids deprotection/protection steps. In contrast to conventional iodine(III) chemistry, our application confirms that hypervalent iodine reagents can also successfully be employed in oxidations of multifunctional substrates. The products should prove useful as enantiomerically pure building blocks in natural product syntheses, in particular the O-benzylated derivatives which are set up for carbanion chemistry.

Scheme 2



Experimental Section

General Methods. All temperatures quoted are uncorrected. Optical rotations were measured in a Perkin-Elmer 141 polarimeter. Infrared spectra were obtained using a Perkin-Elmer 399 spectrophotometer. ^1H-NMR and ^{13}C-NMR spectra were recorded on Bruker AC 250P or AMX 400 spectrometer, respectively. ^{13}C-NMR multiplities were determined by the DEPT-135 method. Tetramethylsilane (TMS) was used as internal standard. All solvents used were reagent grade and were further dried. Reactions were monitored by TLC on silica gel 60 PF^{254} (E. Merck, Darmstadt) and either detected by UV absorption or by charring with 5% H_2SO_4 in ethanol. Preparative column chromatography was performed on silica gel 60 (E. Merck, Darmstadt). Powdered molecular sieves (3 Å) were purchased from Janssen Chemical Co. and may not be replaced by 4 or 10 Å sieves. The following lipases were used: PS from *Pseudomonas fluorescens* (Amano Pharmaceutical Co.), CC from *Candida cylindracea* (Sigma Chem. Co.), and OF (Meito Sangyo Co., Ltd.). [Hydroxy(tosyloxy)-iodo]benzene (**1**) was obtained according to Koser's procedure.[22]

Preparations of Glycals. Glycals **2a** and **10** were purchased from E. Merck, Darmstadt. **4**, **14**, and **17** were obtained by zinc-promoted reductive elimination of the corresponding per-O-acytelated anomeric bromides.[23] Partially acetylated glycals like **2b** were prepared following Holla's description[13] and were obtained as pure compounds after column chromatography on silica gel (PE:EE 1:1) in yields well above 90%. Per-O-benzylated glycals **5**, **11**, **15**, and **18** were synthesized according to the literature[24] by catalytic phase transfer benzylation of the corresponding per-O-acetylated derivatives. **19** was obtained as described by Fraser-Reid.[25]

(18) Lichtenthaler, F. W.; Rönninger, S.; Jarglis, P. *Liebigs Ann. Chem.* **1989**, 1153.
(19) (a) Ferrier, R. J.; Ciment, D. M. *J. Chem. Soc. C* **1966**, 441. (b) Ferrier, R. J.; Prasad, N. *Ibid.* **1969**, 570 and 575.
(20) Ito, Y.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.
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(22) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1976**, *41*, 3609.
(23) Iselin, B.; Reichstein, T. *Helv. Chim. Acta* **1944**, *27*, 1146.
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4,6-Di-*O*-acetyl-1,5-anhydro-3-*O*-benzoyl-2-deoxy-D-*arabino*-hex-1-enitol (2c). To a solution of **2b** (1.0 g, 4.34 mmol) in pyridine (5 mL) at 0 °C were added benzoyl chloride (2.5 mL). The resulting solution was allowed to warm and was then stirred for 16 h. Aqueous workup and column chromatography (petroleum ether/ethyl acetate 4:1) afforded the title compound (1.14 g, 3.4 mmol, 78%): colorless oil; $[\alpha]^{19}_D$ −126.6 °C (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.2−7.4 (m, 5H), 6.51 (dd, 1H, *J* = 6.2, 1.7 Hz), 5.56 (ddd, 1H, *J* = 1.7, 3.4, 5.9 Hz), 5.44 (dd, 1H, *J* = 5.9, 7.7 Hz), 5.00 (dd, 1H, *J* = 3.4, 6.2 Hz), 4.51 (dd, 1H, *J* = 5.9, 12.1 Hz), 4.35 (ddd, 1H, *J* = 3.0, 5.9, 7.7 Hz), 4.26 (dd, 1H, *J* = 3.0, 12.1 Hz), 2.10, 2.07 (2s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.7, 169.5, 165.9, 145.7, 133.3, 129.7, 129.6, 128.5, 99.1, 74.0, 68.2, 67.1, 61.5, 20.8, 20.7. Anal. Calcd for $C_{17}H_{18}O_7$: C, 61.07; H 5.43. Found: C, 61.31; H, 5.33.

4,6-Di-*O*-acetyl-1,5-anhydro-3-*O*-(methoxymethyl)-2-deoxy-D-*arabino*-hex-1-enitol (2d). To a solution of **2b** (1 g, 4.34 mmol) in CH_2Cl_2 (30 mL) at 0 °C were added diisopropylethylamine (4.4 mL, 26 mmol) and dropwise methoxymethyl chloride (0.96 mL, 13 mmol). The resulting solution was allowed to warm and was then stirred for 20 h at 40 °C. Aqueous workup and column chromatography (petroleum ether/ethyl acetate 1:1) afforded the title compound (1.05 g, 3.81 mmol, 88%): colorless oil; $[\alpha]^{20}_D$ −17.7° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 6.42 (d, 1H, *J* = 6.2 Hz), 5.16 (t, 1H, *J* = 6.0 Hz), 4.91 (dd, 1H, *J* = 6.2, 3.3 Hz), 4.69 (s, 2H), 4.42 (dd, 1H, H-6, *J* = 6.0, 11.2 Hz), 4.27−4.10 (m, 3H), 3.75 (s, 3H), 2.10 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.6, 169.7, 144.1, 100.2, 95.2, 73.9, 69.6, 68.4, 61.7, 55.7, 20.9, 20.7. Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H 6.61. Found: C, 52.57; H, 6.58.

4,6-Di-*O*-acetyl-1,5-anhydro-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*arabino*-hex-1-enitol (2f). *tert*-Butyldimethylsilyl chloride (0.33 g, 2.17 mmol) was added to a solution of **2b** (0.5 g, 2.17 mmol) and imidazole (0.44g, 3.26 mmol) in DMF (3 mL) at 0 °C. The resulting solution was allowed to warm and was then stirred for 20 h. Pentane extraction followed by aqueous workup and column chromatography (petroleum ether/ethyl acetate 7.5:1) afforded the title compound (0.6 g, 1.74 mmol, 80%): colorless oil; $[\alpha]^{20}_D$ −30.4° (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, 1H, *J* = 6.1 Hz), 4.97 (dt, 1H, *J* = 1.6, 5.6 Hz), 4.67 (dd, 1H, *J* = 3.1, 6.1 Hz), 4.34 (dd, 1H, *J* = 6.2, 11.8 Hz), 4.12 (ddd, 1H, *J* = 3.2, 5.6, 6.2 Hz), 4.08 (dd, 1H, *J* = 3.2, 11.8 Hz), 4.11 (m, 1H), 2.0 (s, 6H), 0.79 (s, 9H), 0.0 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.5, 143.1, 102.9, 74.0, 70.3, 65.0, 62.0, 25.6, 20.8, 20.7, 17.9, −4.6, −5.0. Anal. Calcd for $C_{16}H_{28}O_6Si$: C, 55.79; H, 8.19. Found: C, 55.41; H, 8.21.

3,6-Di-*O*-acetyl-1,5-anhydro-4-*O*-(methoxymethyl)-2-deoxy-D-*arabino*-hex-1-enitol (7). To a solution of **6** (1.0 g, 4.38 mmol) in CH_2Cl_2 (30 mL) at 0 °C were added diisopropylethylamine (4.4 mL, 26.0 mmol) and dropwise methoxymethyl chloride (0.96 mL, 13.0 mmol). The resulting solution was allowed to warm and was then stirred for 24 h. Aqueous workup and column chromatography (petroleum ether/ethyl acetate 5:1) afforded the title compound (0.66 g, 2.4 mmol, 55%): colorless oil; $[\alpha]^{20}_D$ −36.8° (*c* 1.05, $CHCl_3$); ^1H NMR (C_6D_6) δ 6.15 (dd, 1H, *J* = 6.0 Hz, *J* = 1.2 Hz), 5.48 (m, 1H), 4.73 (dd, 1H, *J* = 3.2, 6.0 Hz), 4.54, 4.43 (2d, 2H, *J* = 6.8 Hz), 4.33 (dd, 1H, *J* = 5.2, 12.0 Hz), 4.30 (dd, 1H, *J* = 3.2, 12.0 Hz), 3.97 (dd, 1H, *J* = 3.2, 5.2, 7.8 Hz), 3.92 (ddd, 1H, *J* = 5.6, 7.8 Hz), 3.09 (s, 3H), 1.68, 1.64 (2s, 6H); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.4, 145.5, 99.0, 96.7, 74.9, 71.7, 69.1, 62.2, 56.1, 21.1, 20.8. Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.61. Found: C, 52.89; H, 6.50.

3,6-Di-*O*-acetyl-1,5-anhydro-4-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*arabino*-hex-1enitol (8). *tert*-Butyldimethylsilyl chloride (0.65 g, 4.34 mmol) was added to a solution of **6** (1.0 g, 4.34 mmol) and imidazole (0.44 g, 6.51 mmol) in DMF (5 mL) at 0 °C. The resulting solution was allowed to warm and was then stirred for 48 h. Aqueous workup followed by column chromatography (petroleum ether/ethyl acetate 8:1) afforded the title compound (1.28 g, 3.71 mmol, 85.3%): crystals; mp 53 °C; $[\alpha]^{20}_D$ −29.9° (*c* 1, $CHCl_3$); ^1H NMR (C_6D_6) δ 6.06 (dd, 1H, *J* = 1.2, 6.0 Hz), 5.29 (ddd, 1H, *J* = 1.2, 2.4, 6.6 Hz), 4.69 (dd, 1H, *J* = 2.4, 6.0 Hz), 4.44 (dd, 1H, *J* = 2.6, 12.0 Hz), 4.14 (dd, 1H *J* = 4.8, 12.0 Hz), 4.02 (dd, 1H, *J* = 6.6, 9.2 Hz), 3.67 (ddd, 1H, *J* = 2.6, 4.8, 9.2 Hz), 1.67, 1.60 (2s, 6H), 0.85 (s, 9H), 0.0, −0.1 (2s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 169.8, 145.7, 99.9, 76.9, 73.2, 67.8, 62.6, 25.8, 20.8, 20.3, 18.2, −4.2, −5.1. Anal. Calcd for $C_{16}H_{28}O_6Si$: C, 55.79; H, 8.19. Found: C, 55.71; H, 8.10.

3,4-*Di*-*O*-acetyl-1,5-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*lyxo*-hex-1-enitol (12). *tert*-Butyldimethylsilyl chloride (2.8 g, 18.7 mmol) was added to a solution of D-galactal (2.5 g, 17 mmol) and imidazole (1.74 g, 25.5 mmol) in freshly distilled anhydrous DMF (150 mL) at 0 °C. The resulting solution was allowed to warm and was then stirred for 16 h. Aqueous workup followed by acetylation of the crude oil with Ac_2O/pyridine and workup under standard conditions and finally purification by column chromatography (petroleum ether/ethyl acetate 3.5:1) afforded the title compound (4.8 g, 13.9 mmol, 82%): colorless oil; $[\alpha]^{22}_D$ −25.2° (*c* 1, $CHCl_3$); ^1H NMR (C_6D_6) δ 6.41 (dd, 1H, *J* = 2.0, 6.2 Hz), 5.54 (ddd, 1H, *J* = 2.0, 2.8, 5.2 Hz), 5.46 (dt, 1H, *J* = 1.6, 5.2 Hz), 4.61 (dt, 1H, *J* = 2.8, 6.2 Hz), 4.03 (dt, 1H, *J* = 1.6, 6.8 Hz), 3.72 (dd, 1H, *J* = 6.4, 10.2 Hz), 3.63 (dd, 1H, *J* = 7.0, 10.2 Hz), 2.09, 1.98 (2s, 6H), 0.72 (s, 9H), 0.01, 0.0 (2s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.3, 170.1, 145.5, 98.8, 75.7, 64.6, 63.2, 60.9, 25.8, 20.9, 20.7, 18.3, −5.1, −5.4. Anal. Calcd for $C_{16}H_{28}O_6Si$: C, 55.79; H, 8.19. Found: C, 55.71; H, 8.10.

4-*O*-Acetyl-1,5-anhydro-3,6-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*lyxo*-hex-1-enitol (13). Reaction conditions were identical with those described for the preparation of **12** except that 3 equiv of imidazole and 2.2 equiv of TBDMS chloride were employed. **13** was isolated in 83% yield: colorless oil; $[\alpha]^{20}_D$ −34.5° (*c* 1, $CHCl_3$); ^1H NMR (C_6D_6) δ 6.34 (dd, 1H, *J* = 1.4, 6.4 Hz), 5.31 (dt, 1H, *J* = 1.4, 4.6 Hz), 4.65 (ddd, 1H, 1.6, 2.4, 6.4 Hz), 4.49 (m, 1H), 4.08 (t, 1H, *J* = 6.4 Hz), 3.83 (dd, 1H, *J* = 7.0, 10.8 Hz), 3.69 (dd, 1H, *J* = 6.0, 10.8 Hz), 2.11 (s, 3H), 0.90, 0.89 (2s, 18H), 0.1, 0.06 (2s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 170.1, 143.6, 103.4, 77.2, 76.3, 63.2, 61.4, 25.9, 25.7, 21.0, 18.3, 18.2, −5.0, −5.1, −5.4, −5.5. Anal. Calcd for $C_{20}H_{40}O_5Si_2$: C, 57.66; H, 9.69. Found: C, 57.81; H, 9.75.

1,5-Anhydro-3,4-bis-O-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-*erythro*-hex-1-enitol (16). *tert*-Butyldimethylsilyl chloride (2.8 g, 18.5 mmol) was added to a solution of L-rhamnal (1.2 g, 9.23 mmol) and imidazole (1.9 g, 27.7 mmol) in DMF (11 mL) at 0 °C. The resulting solution was allowed to warm and was then stirred for 3d. Pentane extraction followed by flash chromatography (petroleum ether/ethyl acetate 50:1) afforded the title compound (2.2 g, 6.1 mmol, 66%): colorless oil; $[\alpha]^{20}_D$ +56.4° (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.28 (d, 1H, *J* = 6.2 Hz), 4.65 (dd, 1H, *J* = 6.2, 3.2 Hz,), 4.08 (bt, 1H), 3.93 (dq, 1H, *J* = 6.4 Hz), 3.56 (dd, 1H, *J* = 5.1, 6.4 Hz), 1.32 (d, 3H, *J* = 6.4 Hz), 0.9 (s, 18H), 0.12, 0.1, 0.09, 0.085 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 102.9, 75.2, 74.7, 69.3, 26.0, 25.9, 18.2, 18.1, 17.2, −3.7, −3.9, −4.2, −4.3. Anal. Calcd for $C_{18}H_{38}O_3Si_2$: C, 60.28; H, 10.68. Found: C, 59.98; H, 10.82.

General Procedure for the Preparation of 2,3-Dihydro-4*H*-pyran-4-ones. A suspension of glycal (1 equiv) and powdered molecular sieves (3 Å, 0.25 g/mmol of glycal) in absolute acetonitrile (20 mL/mmol) under nitrogen was stirred for 5 min at 0 °C. [Hydroxy(tosyloxy)iodo]benzene (1.2 mol %) was added in one portion, and the temperature was raised to rt. During the following 30 min the suspension turned to yellow and back to colorless. After 75 min the suspension was filtered through a pad of Celite, and the residue was washed with dichloromethane. The combined filtrate and washings were extracted with aqueous $NaHCO_3$ (5 mL/mmol) and brine (5 mL/mmol), dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow oil. This crude product was rapidly purified by flash gel filtration on silica gel, as loss of recovered material was observed when the dihydropyranones were exposed to silica gel for long periods. Alternatively, the glycal and $PhI(OCOCH_3)_2$ (1.2 equiv) were dissolved in dry acetonitrile under nitrogen in the presence of powdered molecular sieves (3 Å). The suspension was stirred for 10 min at rt, and *p*-toluenesulfonic acid (1.2 equiv) was added slowly. The

stirring was continued for another 45–75 min, and finally, the reaction mixture was worked up as described above.

Oxidation of **2a-f** and tri-*O*-acetyl-D-allal (**4**) afforded **(2*R*, 3*R*)-3-acetoxy-2-(acetoxymethyl)-2,3-dihydro-4*H*-pyran-4-one (3)** (**2a**, 52%; **2b**, 33%; **2c**, 37%; **2d**, 57%; **2e**, 69%;[26] **2f**, 74%; **4**, 45%) under the conditions described. Likewise, **10** gave **(−)-(2*R*,3*S*)-3-acetoxy-2-(acetoxymethyl)-2,3-dihydro-4*H*-pyran-4-one (24)** (58%) and **14** gave **(−)-(2*S*,3*S*)-3-acetoxy-2-methyl-2,3-dihydro-4*H*-pyran-4-one (27)** (48%). Spectroscopic data and physical constants for **3**, **24**, and **27** are in agreement with those published by Czernecki, Vijayakumara, and Ville as well as by Paulsen and Bünsch.[10] **32** has been described before by Chapleur as well as by Grynkiewics.[27]

(+)-(2*R*,3*R*)-3-(Benzyloxy)-2-((benzyloxy)methyl)-2,3-dihydro-4*H*-pyran-4-one (20). Oxidation of **5** (0.5 g, 1.2 mmol) and chromatographic purification with petroleum ether/ethyl acetate 6:1 afforded the title compound (0.19 g, 0.59 mmol, 49%): colorless oil; $[\alpha]^{20}_D$ +237° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.33–7.25 (m, 11 H), 5.35 (d, 1H, *J* = 6.0 Hz), 5.05, 4.59, 4.55, 4.51 (4d, 4H, *J* = 11.3 Hz), 4.40 (dt, 1H, *J* = 3.6, 11.4 Hz), 4.21 (d, 1H, *J* = 11.4 Hz), 3.77 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 193.5, 162.3, 137.5, 128.5 – 127.5, 105.1, 81.0, 74.5, 74.1, 73.6, 67.8. Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.64; H, 6.01.

(2*R*,3*R*)-3-Hydroxy-2-(acetoxymethyl)-2,3-dihydro-4*H*-pyran-4-one (21). Oxidation of **6** (0.21 g, 0.91 mmol) and flash chromatography with petroleum ether/ethyl acetate (2:1) afforded the title compound (55 mg, 0.30 mmol, 32%). Alternatively, **21** (0.26 g, 1.4 mmol, 42%) was isolated when **9**[17] (1.4 g, 3.3 mmol) was oxidized under the standard conditions described here: crystals; mp 100–101 °C; ^{1}H-NMR ($CDCl_3$) δ 7.41 (d, 1H, *J* = 5.8 Hz), 5.50 (d, 1H, *J* = 5.8 Hz), 4.62 (dd, 1H, *J* = 1.4, 12.4 Hz), 4.44 (dd, 1H, *J* = 4.2, 12.4 Hz), 4.31 (ddd, 1H, *J* = 1.4, 4.2, 12.8 Hz), 4.27 (d, 1H, *J* = 12.8 Hz), 3.58 (b, 1H), 2.15 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 193.3, 170.5, 164.0, 103.7, 80.7, 67.8, 62.4, 20.7.

(+)-(2*R*,3*R*)-2-(Acetoxymethyl)-3-((methoxymethyl)oxy)-2,3-dihydro-4*H*-pyran-4-one (22). Oxidation of **7** (0.57 g, 2.1 mmol) and chromatographic purification with petroleum ether/ethyl acetate (2:1) afforded the title compound (0.23 g, 1.0 mmol, 48 %): crystals; mp 59 °C; $[\alpha]^{20}_D$ +380.3° (*c* 0.59, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.33 (m, 1 H, *J* = 6.0 Hz), 5.42 (d, 1H, *J* = 6.0 Hz), 5.04, 4.76 (2d, 2H, *J* = 6.8 Hz), 4.55 (dd, 1H, *J* = 2.0, 12.0 Hz), 4.48 (ddd, 1H, *J* = 2.0, 4.0, 12.0 Hz), 4.41 (dd, 1H, *J* = 4.0, 12.0 Hz), 4.40 (d, 1H, *J* = 12.0 Hz), 3.42 (s, 3H), 2.34 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.4, 170.5, 162.1, 105.4, 97.5, 78.2, 71.1, 62.1, 56.5, 20.7. Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.40; H, 6.23.

(+)-(2*R*,3*R*)-2-(Acetoxymethyl)-3-(*tert*-butyldimethylsiloxy)-2,3-dihydro-4*H*-pyran-4-one (23). Oxidation of **8** (0.81 g, 2.35 mmol) and chromatographic purification with petroleum ether/ethyl acetate (8:1) afforded the title compound (0.29 g, 0.97 mmol, 41%): crystals; mp 76–77 °C; $[\alpha]^{22}_D$ +219.4° (*c* 1.9, $CHCl_3$); ^{1}H-NMR (C_6D_6) δ 6.43 (d, 1H, *J* = 5.8 Hz), 5.01 (d, 1H, *J* = 5.8 Hz), 4.43 (dd, 1H, *J* = 2.0, 12.0 Hz), 4.17 (dd, 1H, *J* = 4.4, 12.0 Hz), 4.15 (d, 1H, *J* = 12.4 Hz), 3.85 (ddd, 1H, *J* = 2.0, 4.4, 12.4 Hz), 1.67 (s, 3H), 0.98 (s, 9H), 0.38, 0.02 (2s, 6H); ^{13}C-NMR (C_6D_6) δ 192.2, 168.6, 105.1, 80.2, 70.4, 62.4, 26.0, 20.2, 18.7, −3.6, −4.8. Anal. Calcd for $C_{14}H_{24}O_5$-Si: C, 55.97; H, 8.05. Found: C, 56.12; H, 8.19.

(−)-(2*R*,3*S*)-3-(Benzyloxy)-2-((benzyloxy)methyl)-2,3-dihydro-4*H*-pyran-4-one (25). Oxidation of **11** (2.2 g, 5.28 mmol) and chromatographic purification with petroleum ether/ethyl acetate (6:1) afforded the title compound (0.97 g, 3.0 mmol, 57%); colorless oil; $[\alpha]^{20}_D$ −31.8° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.33–7.25 (m, 11 H), 5.45 (dd, 1H, *J* = 1.4, 6.0 Hz), 5.73, 4.58, 4.52, 4.50 (4d, 4H, *J* = 12.0 Hz), 4.50 (ddd, 1H, *J* = 2.4, 5.2, 7.0 Hz), 3.93 (dd, 1H, *J* = 7.0, 10.4 Hz), 3.77 (dd, 1H, *J* = 5.2, 10.4 Hz), 3.71 (dd, 1H, *J* = 1.4, 2.4 Hz); ^{13}C-NMR ($CDCl_3$): δ 189.4, 162.7, 137.5, 137.0, 128.5–127.8, 105.1, 80.6, 74.2, 73.6, 72.0, 67.6. Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.03; H, 6.27.

(+)-(2*R*,3*S*)-3-(Acetoxymethyl)-2-(*tert*-butyldimethylsiloxy)-2,3-dihydro-4*H*-pyran-4-one (26). Oxidation of **12** (0.75 g, 2.18 mmol) or **13** (125 mg, 0.29 mmol) followed by chromatographic purification with petroleum ether/ethyl acetate (8:1) afforded the title compound (0.27 g, 0.91 mmol, 43%; 64 mg, 0.21 mmol, 72%, respectively): colorless oil; $[\alpha]^{20}_D$ +31.2° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.28 (d, 1H, *J* = 6.2 Hz), 5.50 (d, 1H, *J* = 4.6 Hz), 5.38 (d, 1H, *J* = 6.2 Hz), 4.52 (dt, 1H, = 4.6, 6.0 Hz), 3.87 (dd, 1H, *J* = 6.0, 11.4Hz), 3.81 (dd, 1H, *J* = 4.6, 11.4Hz), 2.10 (s, 3H), 0.81 (s, 9H), 0.0 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ 186.2, 168.9, 161.9, 105.2, 80.6, 62.2, 60.3, 25.5, 20.3, 18.0, −5.6, −6.0. Anal. Calcd for $C_{14}H_{24}O_5$-Si: C, 55.97; H, 8.06. Found: C, 56.03; H, 8.11.

(−)-(2*S*,3*S*)-3-(Benzyloxy)-2-methyl-2,3-dihydro-4*H*-pyran-4-one (28). Oxidation of **15** (0.59 g, 1.9 mmol) and chromatographic purification with petroleum ether/ethyl acetate (7:1) afforded the title compound (0.22 g, 1.0 mmol, 53%): colorless oil; $[\alpha]^{20}_D$ −309° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.33–7.25 (m, 6H), 5.38 (d, 1H, *J* = 5.8 Hz), 5.02, 4.65 (2d, 2H, *J* = 11.6 Hz) 4.46 (dq, 1H, *J* = 9.6, 6.4 Hz), 3.72 (d, 1H, *J* = 9.6 Hz), 1.42 (d, 3H, *J* = 6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 193.3, 162.4, 137.3, 130.1–128.0, 104.9, 78.7, 78.6, 73.9, 17.1. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54, H, 6.47. Found: C, 71.49; H, 6.46.

(−)-(2*S*,3*S*)-3-(*tert*-Butyldimethylsiloxy)-2-methyl-2,3-dihydro-4*H*-pyran-4-one (29). Oxidation of **16** (0.66 g, 1.85 mmol) and chromatographic purification with petroleum ether/ethyl acetate (20:1) afforded the title compound (0.3 g, 1.24 mmol, 67%) within 15 min at −6 °C: colorless oil; $[\alpha]^{17}_D$ −243.5° (*c* 1.16, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.26 (d, 1H, *J* = 6.2 Hz), 5.32 (d, 1H, *J* = 6.2 Hz), 4.29 (dq, 1H, *J* = 6.4, 11.8 Hz), 4.0 (d, 1H, *J* = 11.8 Hz), 1.49 (d, 3H, *J* = 5.6 Hz), 0.91 (s, 9H), 0.21, 0.08 (2s, 6H). Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9,15. Found: C, 59.71; H, 9.23.

(−)-(2*S*,3*R*)-3-Acetoxy-2-methyl-2,3-dihydro-4*H*-pyran-4-one (30). Oxidation of **17** (0.38 g, 1.8 mmol) and chromatographic purification with petroleum ether/ethyl acetate (5:1) afforded the title compound (0.16 g, 0.9 mmol, 50%): crystals; mp 89–90 °C; $[\alpha]^{20}_D$ −41.0° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.32 (d, 1H, *J* = 6.0 Hz), 5.45 (dd, 1H, *J* = 0.8, 6.0 Hz), 5.40 (dd, 1H, *J* = 0.8, 4.0 Hz), 4.68 (dq, 1H, *J* = 4.0, 6.4 Hz), 2.15 (s, 3H), 1.38 (d, 3H, *J* = 6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 187.1, 169.5, 126.6, 105.3, 76.8, 71.0, 20.6, 14.0. Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.40; H, 5.88.

(+)-(2*S*,3*R*)-3-(Benzyloxy)-2-methyl-2,3-dihydro-4*H*-pyran-4-one (31). Oxidation of **18** (1.2 g, 3.87 mmol) and chromatographic purification with petroleum ether/ethyl acetate (10:1) afforded the title compound (0.49 g, 2.24 mmol, 58%): colorless oil; $[\alpha]^{20}_D$ +25.6° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 7.33–7.25 (m, 6H), 5.41 (dd, 1H, *J* = 1.6, 6.0 Hz), 4.77, 4.51 (2d, 2H, *J* = 12 Hz), 4.43 (dq, 1H, *J* = 2.6, 6.8 Hz), 3.50 (dd, 1H, *J* = 1.6, 2.6 Hz), 1.45 (d, 3H, *J* = 6.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 190.7, 163.1, 137.2, 128.5– 128.0, 104.6, 78.2, 76.6, 72.0, 15.0. Anal. Calcd for $C_{13}H_{14}O_3$: C 71.54, H 6.47. Found: C, 71.69; H, 6.57.

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(26) The crude oil obtained from TMSCl/HMDS-promoted silylation of **2b** was directly subjected to the oxidation conditions.

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