107. Thermal and Photochemical Oxetane Formation. A Contribution to the Synthesis of Branched-Chain Aldonolactones[1])

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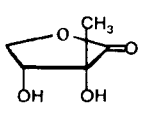
Derivatives of 2-*C*-branched-chain erythrono-1,4-lactones of the type **1** have been synthesized under reductive conditions using DIBAL from the oxetane **2**, which is easily accessible from diethyl mesoxalate (**4**) and 2,2-diisopropyl-1,3-dioxole (**3**) in high yield by means of a catalytic cycloaddition. Similarly, **2** rearranges in presence of $AlMe_3$ under formation of an erythronolactone with an additional branching at C(4). The corresponding oxetanes **7–9** from ethyl pyruvate (**5**) and ethyl trimethylpyruvate (**6**), respectively, have been studied with regard to their reductions yielding building blocks of branched-chain sugars.

1. Introduction. – There are only few reports on naturally occurring branched-chain sugars up to the sixties [2] [3]. However, after the first syntheses of apiose [4] and hamamelose [5] and with the increasing antibiotica research [6] [7], the chemistry and the synthesis of branched-chain carbohydrates and corresponding lactones gained more and more attention [8–11]. The first natural lactone of a branched-chain aldonic acid, 2-*C*-methyl-D-erythrono-1,4-lactone (**1**), has been isolated by *Teresa* [12] from the Iberian milk vetch (*Astragalus lusitanicus* LAM., fam. Leguminosae), although *Lindberg* [13] already synthesized **1** from D-xylose in 1967. There is only one further report on the synthesis of **1** by *Yoshimura et al.* [14].



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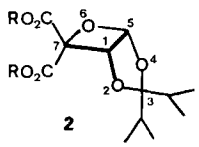

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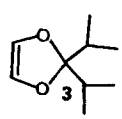

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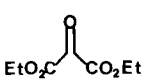

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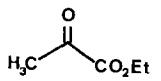

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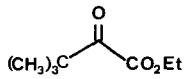

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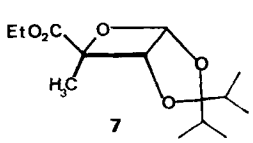

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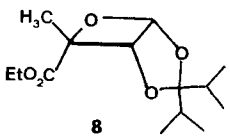

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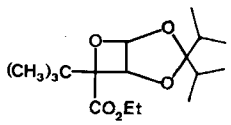

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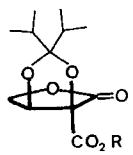
[1]) Part 4 of 'Thermal Reactions of Donor-Acceptor Systems'; for part 3, see [1].

[2]) Taken in part from the Ph.D. thesis (RWTH Aachen 1987). Present address: *J. H. Benecke AG*, Beneckeallee 40, Postfach 709, D–3000 Hannover 1.

Here, we wish to report about a new synthesis of a racemic derivative of **1** and similar branched-chain lactones from the oxetane **2**, the latter being easily accessible from **3** and **4**. Furthermore, we have investigated various reactions of **2** with nucleophiles yielding erythronolactones of the type **1** with an additional branching or functionalization at C(4). For comparison of reactivity, the corresponding oxetanes **7**–**9** have also been studied[3]).

2. Synthesis of Oxetanes. – The oxetane **2** has been synthesized from diethyl mesoxalate (**4**) and 2,2-diisopropyl-1,3-dioxole (**3**) in presence of $ZnCl_2$ as catalyst in 84% yield [15]. The other oxetanes **7**–**9** have been prepared by means of the *Paterno-Büchi* reaction from ethyl pyruvate (**5**) and its trimethyl derivate **6** using the same olefin **3** [15]. Only one stereoisomer was formed from **3** and **6**, the configuration of which has not been assigned yet. A detailed report on the synthesis of these and other oxetanes by means of thermal and photochemical cycloadditions will be published soon [15].

3. Racemic Derivatives of 2-*C*-Methyl-erythrono-1,4-lactone from 2. – The oxetane **2** can be converted to the branched-chain erythronolactone **10** by treatment with diisobutylaluminium hydride (DIBAL) in CH_2Cl_2 at −78°. In a following step, the reduction of the ester group in position 2 of **10** would lead to an acetal derivative of racemic **1**.



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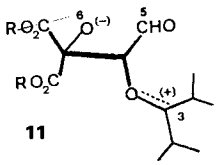

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Although we have not been able to scavenge any intermediate, we assume a mechanism which involves first a coordination of the oxetane O-atom with the metal weakening the C(5)–O(6) and the C(3)–O(4) bonds under formation of an intermediate of the type **11**. Reduction of the aldehyde group in **11** and cyclization would lead to **10**. In order to optimize the yields of **10**, several experiments by varying the reducing agents, the reaction temperature, and the solvents were performed. The results are listed in the *Table*. In spite of the relatively low yield, the reduction with DIBAL in CH_2Cl_2 as solvent at −78° turned out to be the best method.

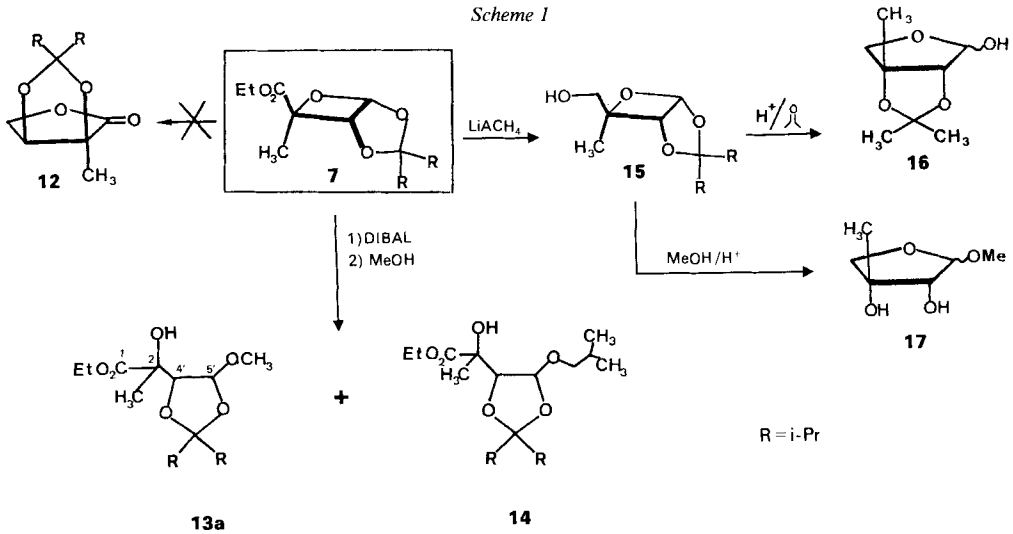
Table. *Optimization of the Formation of the Lactone* **10**

DIBAL	$NaBH_4$	$Li(HAl(OMe)_3)$	9-Borabicyclo[3.3.1]-nonane (9-BBN)	$LiAlH_4$
−78°/CH_2Cl_2	−5°/DMF	0°/THF	0°/THF	−10°/Et_2O
yield 23.6%	yield 20%	no **10**	yield 8%	no **10**
	25°/DMF	10°/THF	−78°/THF	0°/Et_2O
	yield 19%	no **10**	no **10**	no **10**
	−70°/THF			0°/THF
	yield 20%			no **10**

[3]) All structures of synthesized products are racemic, nevertheless, in the formulae only one enantiomer is shown.

4. Reduction of the Oxetanes 7 and 8. – The synthesis of the erythronolactone **1** from **10** would require a selective reduction of the ester group to a Me group. To simplify the synthesis we have studied the reductive rearrangement of **7** or **8** similar to that of **2**. The results using DIBAL and $LiAlH_4$ are shown in *Scheme 1*.

Scheme 1



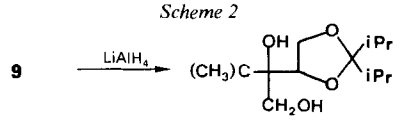
In both cases, a reductive rearrangement of **7** under formation of **12**, the acetal of **1**, has not been observed. Instead, with DIBAL, only reacetalization occurred leading to **13a** and **14**, either from MeOH which was used in the working-up procedure or from i-PrOH (from DIBAL), respectively. Using $LiAlH_4$, however, the reduction of the ester group yielded **15**. This selective process has not been reported before for oxetanes, since reductions generally proceed under cleavage of the oxetane ring [11] [16] [17]. Alcohol **15** is the precursor of the deoxygenated apiose derivatives **16** and **17** which can easily be synthesized in one step from **15** (*cf.* [11] [18]).

Reduction of the stereoisomeric oxetane **8** using DIBAL yielded ethyl 2-(2,2-diisopropyl-5-methoxy-1,3-dioxolan-4-yl)-2-hydroxypropionate (**13b**), a stereoisomer of **13a**.

5. Reduction of Oxetane 9. – The failure of a reductive rearrangement of **7** and **8** to **12** led us to an investigation of the steric influence of bulky substituents in position 7 of oxetanes of the type **2**, **7**, and **8**. Mild reducing agents, *e.g.* $NaBH_4$ or DIBAL, did not attack the oxetane **9** bearing a *tert*-butyl group at C(7). $LiAlH_4$, however, reduced **9** to **18**, but no rearrangement product was found (*Scheme 2*).

From this result, one may assume that only the special substitution pattern of **2** causes the reductive rearrangement in presence of metal hydrides. The replacement of one ester

Scheme 2



group in **2** by another substituent of similar electronic properties, *e.g.* a nitrile group, might give more informations about the influence of electronic effects in this unusual rearrangement. However, experiments to synthesize oxetanes from **3** and ethoxalyl cyanide failed so far.

6. Syntheses of Position-4-Branched-Chain Lactones. – According to our postulated mechanism of the rearrangement, the aldehyde group of the intermediate **11** should also be trapped by other nucleophiles, *e.g.* by organometallic reagents leading to an additional branching in position 4 of the lactone.

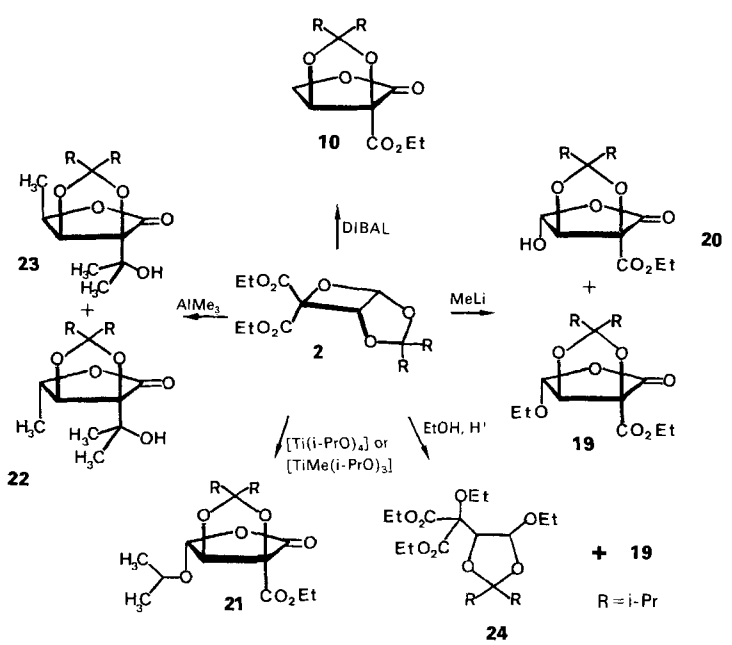
MeMgI as well as BuLi reacted rather unselectively with **2** yielding a complex mixture of products and polymeric material. In both cases, only small amounts of starting material were recovered. The use of MeLi actually caused the rearrangement to the lactone, but the intermediate was scavenged by ethanolate (→**19**) rather than by MeLi. Methyl-branched lactones were not detected (HPLC and GC/MS) and the hydroxy-substituted by-product **20** may be formed by hydrolysis in the workup procedure.

The more selective reagent, methyltitaniumtriisopropylate [19] also failed in transforming **2** to the expected lactone with a Me group at C(4). On the contrary, isopropylate was incorporated leading to **21**, which is also accessible from **2** and titanium tetraisopropylate, even in higher yields.

We only succeeded in producing a C(4)-branched-chain unit by means of the highly reactive $AlMe_3$. The two diastereoisomeric 4-*C*-Me-substituted lactones **22** and **23** were formed in a 1:5 ratio upon treating **2** with $AlMe_3$ in CH_2Cl_2 at 0°.

It should be noted that under acid catalysis weak nucleophiles such as EtOH also caused the rearrangement of **2** to the lactone **19**, beside the cleavage of the oxetane ring under formation of **24**.

Scheme 3



7. Structures of the Products. – The structures of the products have been assigned spectroscopically by means of ^{1}H-NMR, ^{13}C-NMR, MS, and IR measurements. However, it was not possible to perform the complete configurational assignments for **9** since only one isomer has been isolated. The configuration of the substituents at C(4) of the lactones was determined on the basis of the coupling of H–C(3) with H–C(4). For example, $J(4,3)$ of **23** is 3.5 Hz, whereas **22** shows a *s* for H–C(3) and a *q* for H–C(4) (coupling with Me group) [4] [18] [20]. The *'exo'*- and *'endo'*-configuration of the oxetanes **7** and **8** were assigned by means of ^{13}C-NMR spectroscopy: the CH_3–C(7) of **7** is shifted upfield by 6.3 ppm [15] because of its *γ-syn*-interaction with the corresponding O-atom [21].

Experimental Part

1. *General.* The starting materials were synthesized according to methods described in the literature: Diethyl 2-oxopropanedioate (**4**) [22], ethyl 3,3-dimethyl-2-oxobutyrate (**6**) [23], ethoxalyl cyanide [24] and 2,2-diisopropyl-1,3-dioxole (**3**) [25]. Ethyl 2-oxopropanoate (**5**) was purchased from *Janssen* and distilled before use. Methyltitanium triisopropylate was synthesized according to procedures reported by *Reetz et al.* [19] and *Seebach et al.* [26]. The solvents were purified by standard methods [27]. All glass apparatus were immersed in an aq. NaOH soln. over night in order to prevent acid-catalyzed side reactions. GC: *Carlo Erba Fractovap 2101* using the *OV 101* column (5% on *Chromosorb WAW DMCS*, 80/100 mesh.) HPLC: *Gilson-303* chromatograph and *Chromosorb Si 60* columns, mixtures of AcOEt in cyclohexane. Flash chromatography (FC): Silica gel *60* (0.04–0.063 mm) from *Macherey & Nagel.* IR spectra: *Perkin-Elmer 377, Perkin-Elmer 1700.* ^{1}H-NMR and ^{13}C-NMR spectra: *Varian EM 390* (90 MHz). *Varian VXR 300* (300 MHz), *Varian CFT 20* (20 MHz), *Varian VXR 300* (75 MHz). GC/MS spectra: *Varian MAT 212.*

2. *Reduction of* **2** *with DIBAL.* To a soln. of **2** (3.3 g, 0.01 mol) in CH_2Cl_2 (130 ml), DIBAL (1.4 equiv. in CH_2Cl_2, −78°) was added and stirred for 1 h. After quenching with MeOH and addition of a soln. of sodium tartrate and H_2O, the product was extracted (CH_2Cl_2) and purified by HPLC (AcOEt/C_6H_{12} 25:75).

*2,3-O-(2',4'-Dimethylpentan-3'-ylidene)-2-C-(ethoxycarbonyl)-*DL*-erythrono-1,4-lactone* (**10**): Yield 23.6%, colourless oil. IR ($CDCl_3$): 1790, 1725 (C=O), 1380 (i-Pr). ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.88, 0.96 (2*d*, J = 7, $(CH_3)_2$CH); 1.03 (*s*, $(CH_3)_2$CH); 1.31 (*t*, J = 7.2, CH_3CH_2O); 2.14–2.18 (*m*, 2 $(CH_3)_2CH$); 4.32 (*q*, J = 7.2, CH_3CH_2O); 4.49 (*d*, J = 2.2, CH_2(4)); 4.98 (*t*, J = 2.2, CH(3)). ^{13}C-NMR ($CDCl_3$, 20 MHz): 14.0 (CH_3CH_2O); 16.9, 17.5 (2 $(CH_3)_2$CH); 32.8, 34.9 (2 $(CH_3)_2CH$); 63.0 (CH_3CH_2O); 71.3 (C(4)); 81.5 (C(3)); 85.3 (C(2)); 124.4 (O–C–O); 165.8, 171.2 (CO_2Et, C(1)). MS: 286 (0.1, $M^{+\cdot}$), 287 (94.8), 243 (8.9), 143 (15.1), 97 (9.1), 71 (90.6), 55 (10.1), 43 (100), 41 (11.6).

3. *Reduction of* **7** *with DIBAL.* See *Exper. 2;* HPLC: AcOEt/C_6H_{12} 15:85.

Ethyl 2-(2',2'-Diisopropyl-5'-methoxy-1',3'-dioxolan-4'-yl)-2-hydroxypropionate (**13a**): Yield 19%, colourless oil. IR (CCl_4): 3510 (OH), 1730 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.8–1.1 (*m*, 2 $(CH_3)_2$CH); 1.3 (*t*, J = 7.5 Hz, CH_3CH_2O); 1.39 (*s*, CH_3(3)); 1.7–2.3 (*m*, 2 $(CH_3)_2CH$); 3.36 (*s*, CH_3O); 3.89 (*d*, J = 5.4, CH(4')); 4.18 (*q*, J = 7.5, CH_3CH_2O); 4.9 (*d*, J = 5.4, CH(5')). ^{13}C-NMR (C_6D_6, 20 MHz): 14.0 (CH_3CH_2O); 17.1, 17.7, 17.9, 18.3 (2 $(CH_3)_2$CH); 22.7 (C(3)); 33.9, 35.2 (2 $(CH_3)_2CH$); 56.2 (CH_3O); 62.0 (CH_3CH_2O); 74.4 (C(2)); 86.9 (C(4)); 104.2 (C(5')); 117.8 (C(2')); 174.8 (C(1)). MS: 303 (0.03, $M^{+\cdot}$ − 1), 262 (8), 261 (58), 174 (9), 173 (100), 145 (36), 131 (9), 117 (10), 115 (18), 85 (9.5), 74 (14), 71 (90), 43 (56), 41 (9).

Ethyl 2-[2',2'-Diisopropyl-5'-(2-methylpropyl)-1',3'-dioxolan-4'-yl]-2-hydroxypropionate (**14**): Yield 43%, colourless oil. IR (CCl_4): 3510 (OH), 1730 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.8–1.09 (*m*, 2 $(CH_3)_2$CH, $(CH_3)_2CHCH_2$); 1.28 (*t*, J = 7.5, CH_3CH_2O); 1.40 (*s*, CH_3(3)); 1.6–2.35 (*m*, 2 $(CH_3)_2CH$, $(CH_3)_2CHCH_2$); 3.15, 3.50 (2 *dd*, J = 9, 7, $(CH_3)_2CHCH_2$); 3.36 (*s*, OH); 3.93 (*d*, J = 5, CH(4')); 4.17 (*q*, J = 7.5, CH_3CH_2O); 5.02 (*d*, J = 5, CH(5')). ^{13}C-NMR (CCl_4, C_6D_6, 20 MHz): 14.0 (CH_3CH_2O); 17.7, 17.9, 17.9, 18.3 (2 $(CH_3)_2$CH); 19.5 ($(CH_3)_2CHCH_2$); 22.8 (C(3)); 28.8 ($(CH_3)_2CHCH_2$); 33.8, 35.2 (2 $(CH_3)_2CH$); 62.0 (CH_3CH_2O); 74.4 (C(2)); 76.1 ($(CH_3)_2CHCH_2$); 86.9 (C(4')); 103.1 (C(5')); 117.6 (C(2')); 174.8 (C(1)). MS: 345 (0.03, $M^{+\cdot}$ − 1), 303 (45), 229 (8), 216 (64), 159 (43), 131 (22), 115 (20), 87 (9), 71 (100), 57 (37), 43 (55), 41 (19).

4. *Reduction of* **7** *with* $LiAlH_4$. To a suspension of $LiAlH_4$ in Et_2O, **7** was slowly added. After stirring for 2 h, the mixture was refluxed for 1 h. The product was isolated by HPLC (AcOEt/C_6H_{12} 15:85) after workup.

3,3-Diisopropyl-7-'endo'*-methyl-2,4,6-trioxabicyclo[3.2.0]heptane-7-*'exo'*-methanol* (**15**): Yield 19%, white solid. M.p. 51°. IR ($CDCl_3$): 3560 (OH), 1385 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.9, 0.95, 1.05, 1.1 (4 *d*, *J* = 7, 2 (CH_3)$_2$CH); 1.25 (*s*, CH_3–C(7)); 1.9–2.3 (*m*, 2 (CH_3)$_2$C*H*); 2.5 (*s*, OH); 3.45, 3.78 (2 *d*, *J* = 8.1, CH_2OH); 4.0 (*d*, *J* = 3.9, H–C(1)); 5.75 (*d*, *J* = 3.9, H–C(5)). ^{13}C-NMR (C_6D_6, 20 MHz): 17.9, 18.07, 18.14, 18.3 (2 (CH_3)$_2$CH); 24.0 (CH_3–C(7)); 34.3, 35.6 (2 (CH_3)$_2$*C*H); 76.3 (CH_2OH); 76.7 (C(7)); 85.4 (C(1)); 106.5 (C(5)); 119.7 (C(3)). MS: 231 (0.01, M^+), 187 (46), 169 (20), 115 (10), 99 (51), 71 (100), 43 (69), 41 (11).

5. *Product of* **8** *with DIBAL.* Yield of **13b**, 17%; colourless oil. IR (CCl_4): 3540 (OH), 1740 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.8–1.0 (*m*, 2 (CH_3)$_2$CH); 1.26 (*s*, CH_3(3)); 1.27 (*t*, *J* = 7, CH_3CH_2O); 1.80–2.27 (*m*, 2 (CH_3)$_2$C*H*); 3.13 (*s*, OH); 3.43 (*s*, CH_3O); 3.92 (*d*, *J* = 5.4, CH(4')); 4.23 (*dq*, *J* = 11, 7, CH_3CH_2O); 5.0 (*d*, *J* = 5.4, CH(5')). ^{13}C-NMR (C_6D_6, 20 MHz): 14.1 (CH_3CH_2O); 17.8, 17.9, 18.0, 18.3 (2 (CH_3)$_2$CH); 21.8 (C(3)); 33.8, 35.3 (2 (CH_3)$_2$*C*H); 56.2 (CH_3O); 61.9 (CH_3CH_2O); 74.2 (C(2)); 86.3 (C(4')); 104.2 (C(5')); 117.6 (C(2')); 174.9 (C(1)).

6. *Reduction of* **9** *with LiAlH*$_4$. See *Exper. 4*; HPLC: AcOEt/C_6H_{12} 25:75.

2-(2',2'-Diisopropyl-1',3'-dioxolan-4'-yl)-3,3-dimethylbutane-1,2-diol (**18**): Yield 72.6%, colourless oil. IR ($CDCl_3$): 3490 (OH), 1375 (*d*, i-Pr, *t*-Bu). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.93–0.97 (*m*, 2 (CH_3)$_2$CH); 1.01 (*s*, *t*-Bu); 2.09, 2.10 (2 *sept.*, *J* = 7, 2 (CH_3)$_2$C*H*); 2.86 (*s*, OH); 3.50, 3.66 (2*d*, *J* = 11.5, CH_2OH); 3.92 (*dd*, *J* = 10, 8.5, 1 H–C(5')); 4.06 (*dd*, *J* = 8.5, 5.5, 1 H–C(5')); 4.29 (*dd*, *J* = 10, 5.5, CH(4')). ^{13}C-NMR ($CDCl_3$, 75 MHz): 17.6, 17.8, 17.9, 18.1 (2 (CH_3)$_2$CH); 26.1 ((CH_3)$_3$C); 34.2, 34.6 (2 (CH_3)$_2$*C*H); 37.7 ((CH_3)$_3$*C*); 63.0 (C(1)); 67.4 (C(5')); 75.9 (C(2)); 79.4 (C(4')); 114.2 (C(2')). MS: 272 (0.14, $M^+ - 2$), 271 (1), 156 (2), 127 (4), 113 (35), 97 (7), 85 (18), 71 (78), 57 (61), 55 (22), 43 (100), 41 (32). Anal. calc. for $C_{15}H_{30}O_4$ (274.4): C 65.66, H 11.02; found: C 65.58, H 10.85.

7. *Reaction of* **2** *with MeLi.* To 42 mmol of MeLi in 20 ml of Et_2O, 9.7 mmol of **2** in 10 ml of Et_2O were added (–17°). After stirring for 2 h (–17°), the suspension was hydrolyzed with MeOH/H_2O 1:3 and worked up. After filtration (Al_2O_3), 3 compounds were isolated by HPLC (AcOEt/C_6H_{12} 4:6), of which one was identified as unreacted **2** (28%).

*2,3-*O*-(2',4'-Dimethylpentan-3'-ylidene)-2-*C*-(ethoxycarbonyl)-4-*C*-hydroxy-*DL*-erythrono-1,4-lactone* (**20**): Yield 8.7%, colourless oil. IR (CCl_4): 3450 (OH), 1790, 1730 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.82–1.15 (*m*, 2 (CH_3)$_2$CH); 140 (*t*, *J* = 7.5, CH_3CH_2O); 1.9–2.4 (*m*, 2 (CH_3)$_2$C*H*); 4.37 (*q*, *J* = 7.5, CH_3CH_2O); 4.65 (*s*, H–C(3)); 4.75 (*s*, OH); 5.70 (*s*, H–C(4)). MS: 261 (0.18, $M^+ - 41$), 259 (6), 215 (7), 97 (3), 71 (100), 55 (11), 44 (18), 43 (96), 41 (18), 40 (19).

*2,3-*O*-(2',4'-Dimethylpentan-3'-ylidene)-4α-*C*-ethoxy-2-*C*-(ethoxycarbonyl)-*DL*-erythrono-1,4-lactone* (**19**): Yield 31%, colourless oil. IR (CCl_4): 1800, 1735 (C=O), 1375 (*d*, i-Pr). ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.87–1.03 (*m*, 2 (CH_3)$_2$CH); 1.26, 1.28 (2*t*, *J* = 7.5, 2 CH_3CH_2O); 2.0–2.33 (*m*, 2 (CH_3)$_2$C*H*); 3.4–4.05 (*m*, CH_3CH_2O–C(4)); 4.30 (*q*, *J* = 7.5, $CH_3CH_2O_2C$); 4.67 (*s*, CH(3)); 5.47 (*s*, CH(4)). ^{13}C-NMR ($CDCl_3$, 20 MHz): 13.9–14.8 (2 CH_3CH_2O); 16.9, 17.1 ((CH_3)$_2$CH); 17.4 ((CH_3)$_2$CH); 32.7, 34.9 (2 (CH_3)$_2$*C*H); 62.8, 65.9 (2 CH_3CH_2O); 85.4 (C(3)); 104.4 (C(4)); 124.9 (O–C–O), 171.1 (C(1)). MS: 331 (0.03, $M^+ + 1$), 288 (10), 287 (74), 189 (6), 99 (39), 71 (100), 43 (52), 41 (8).

8. *Reaction of* **2** *with a Cation-Exchange Resin.* To a soln. of **2** in EtOH was added *Lewatit SC 104* (exchange resin). After stirring for 36 h (25°), the suspension was worked up. The product was separated by HPLC (AcOEt/C_6H_{12} 15:85) giving **19** (45%) and **24** (55%).

Diethyl 2-Ethoxy-2-(5'-ethoxy-2',2'-diisopropyl-1',3'-dioxolan-4'-yl)-malonate (**24**): Colourless oil. IR (CCl_4): 1740 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.8–1.45 (*m*, 4 CH_3CH_2O, 2 (CH_3)$_2$CH); 1.5–2.3 (*m*, 2 (CH_3)$_2$C*H*); 3.21–3.85 (*m*, 2 CH_3CH_2O, ether); 3.86–4.43 (*m*, 2 CH_3CH_2O, ester); 4.63 (*d*, *J* = 6.6, CH(4')); 4.68 (*d*, *J* = 6.6, CH(4')). ^{13}C-NMR (CCl_4, C_6D_6, 20 MHz): 13.8, 13.9, 15.1, 15.3 (4 CH_3CH_2O); 17.9, 18.1, 18.2, 18.3 (2 (CH_3)$_2$CH); 33.4, 34.7 (2 (CH_3)$_2$*C*H); 60.7, 61.0, 61.2, 61.7 (4 CH_3CH_2O); 81.3 (C(4')); 85.2 (C(2)); 99.9 (C(5')); 118.7 (C(2')); 166.7, 168.6 (C(1), C(3)). MS: 404 (0.11, M^+), 362 (8), 361 (44), 274 (6), 273 (39), 245 (23), 199 (10), 198 (97), 171 (9), 143 (8), 103 (100), 99 (10), 75 (30), 71 (26), 47 (23), 43 (43).

9. *Reaction of* **2** *with Methyltitanium Triisopropylate.* To a soln. of methyltitanium triisopropylate in CCl_4 (0°), **2** in CCl_4 was added within 20 min. After stirring for 5 h (25°), the soln. was worked up with aq. NH_4Cl soln. The mixture was extracted with CH_2Cl_2, dried ($MgSO_4$), and separated by HPLC (AcOEt/C_6H_{12} 25:75).

*2,3-*O*-(2',4'-Dimethylpentan-3'-ylidene)-2-*C*-(ethoxycarbonyl)-4α-*C*-isopropoxy-*DL*-erythrono-1,4-lactone* (**21**): Yield 24%, colourless oil. IR (CCl_4): 1800, 1740 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR (CCl_4, 90 MHz): 0.9–1.13 (*m*, 2(CH_3)$_2$CH–C); 1.39 (*t*, *J* = 7.2, CH_3CH_2O); 1.36 (*s*, 1 CH_3 of i-PrO); 1.49 (*s*, 1 CH_3 of i-PrO); 2.14 (*m*, 2(CH_3)C*H*–C); 3.9–4.4 (*m*, (CH_3)$_2$C*H*–O); 4.3 (*q*, *J* = 7.2, CH_3CH_2O); 4.57 (*s*, CH(3)); 5.5 (*s*, CH(4)). ^{13}C-NMR (C_6D_6, 20 MHz): 13.8 (CH_3CH_2O); 17.1, 17.3 ((CH_3)$_2$CH–C); 17.5 ((CH_3)$_2$CH–C); 21.3, 23.2 ((CH_3)$_2$CH–O); 33.0, 35.1 (2 (CH_3)$_2$*C*H–C); 62.3 (CH_3CH_2O); 72.2 ((CH_3)$_2$*C*H–O); 85.8 (C(3)); 86.0 (C(2)); 103.1 (C(4)); 124.4

(O–C–O); 165.8, 170.1 (CO_2Et, C(1)). MS: 343 (0.04, $M^{+\cdot} - 1$), 302 (8), 301 (52), 185 (4), 113 (27), 71 (100), 43 (50), 41 (7).

10. *Reaction of* **2** *with* $AlMe_3$. To a soln. of **2** in CH_2Cl_2, 5 equiv. of $AlMe_3$ in hexane were added at 0°. After stirring for 4 h at 0° and 10 h at 25°, ice-cold 10% NaOH soln. was added, and the products were extracted with CH_2Cl_2 and separated by HPLC (AcOEt/C_6H_{12} 15:85).

*2,3-O-(2',4'-Dimethylpentan-3'-ylidene)-4α-C-methyl-2-C-(1''-methyl-1''-hydroxyethyl)-*DL*-erythrono-1,4-lactone* (**22**): Yield 75%, colourless oil. IR ($CDCl_3$): 3500 (OH), 1770 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 0.93, 0.97 (2*d*, J = 7, $(CH_3)_2$CH); 1.02 (*d*, J = 7, $(CH_3)_2$CH); 1.42 (*s*, CH_3–C(1'')); 1.48 (*d*, J = 7, CH_3–C(4)); 1.50 (*s*, CH_3–C(1'')); 1.95, 2.08 (2 *sept.*, J = 7, 2 $(CH_3)_2CH$); 4.30 (*s*, CH(3)); 4.52 (*q*, J = 7, CH(4)); 4.54 (*s*, OH). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 18.1, 18.25, 18.3, 18.5, 18.6 (2 $(CH_3)_2$CH, CH_3–C(4)); 25.7, 26.7 (2 CH_3–C(1'')); 34.6, 35.3 (2 $(CH_3)_2CH$); 71.5 (C(1'')); 80.4 (C(3)); 83.1 (C(4)); 90.4 (C(2)); 119.0 (O–C–O); 175.3 (C(1)). MS: 286 (0.03, $M^{+\cdot}$), 244 (7), 243 (52), 71 (100), 59 (6), 43 (37), 41 (5).

*2,3-O-(2',4'-Dimethylpentan-3'-ylidene)-4β-C-methyl-2-C-(1''-methyl-1''-hydroxyethyl)-*DL*-erythrono-1,4-lactone* (**23**): Yield 14%, colourless oil. IR (CCl_4): 3480 (OH), 1780 (C=O), 1380 (*d*, i-Pr). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.97, 0.98, 1.02, 1.03, (4*d*, J = 7, 2 $(CH_3)_2$CH); 1.34, 1.47 (2*s*, 2 CH_3–C(1'')); 1.48 (*d*, J = 6.5, CH_3–C(4)); 2.02, 2.11 (2 *sept.*, J = 7, 2 $(CH_3)_2CH$); 2.14 (*s*, OH); 4.54 (*dq*, J = 3.5, 6.5, CH(4)); 4.61 (*d*, J = 3.5, CH(3)). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.6 (CH_3–C(4)); 18.0, 18.05, 18.1, 18.2 (2 $(CH_3)_2$CH); 24.3, 26.0 (2 CH_3–C(1')); 34.1, 34.7 (2 $(CH_3)_2CH$); 71.2 (C(1')); 76.1 (C(3)); 79.4 (C(4)); 91.1 (C(2)); 118.8 (O–C–O); 174.8 (C(1)). MS: 271 (0.06, $M^{+\cdot} - 15$), 243 (4), 111 (3), 72 (4), 71 (100), 59 (11), 43 (64), 41 (9).

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