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MCPBA Oxidation of Bicyclo[3.3.0]octane-3,7-dione: an Easy Entry to a New Functionalized Cyclopentanoid Building Block °#

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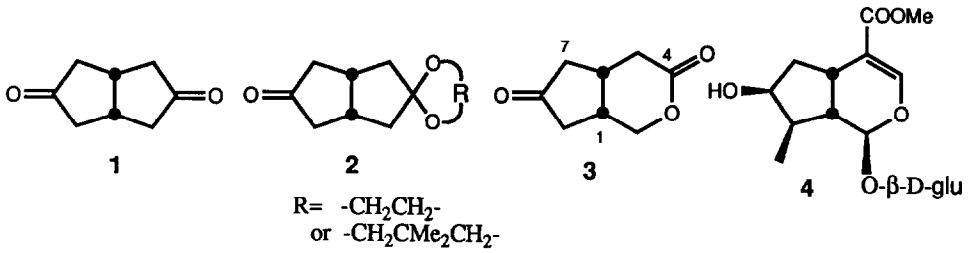
Abstract. Alteration of the C_{2V} symmetry of *cis*-bicyclo[3.3.0]octane-3,7-dione was achieved by a MCPBA controlled Baeyer-Villiger oxidation. *Cis*-3-oxabicyclo[4.3.0] nonane-4,8-dione (**3**) thus obtained was used in a formal synthesis of (±)-loganin (**4**).

INTRODUCTION

Cis-bicyclo[3.3.0]octane-3,7-dione (**1**), a commercial product easily available on a large scale from the Weiss reaction,[1] represents a valuable building block for the construction of cyclopentane derivatives, as shown by the synthesis of carboprostacyclines (carbocyclines),[2] iridoids,[3] sesquiterpenoids [4] and poliquinanes.[5]



However, the high C_{2V} symmetry of compound **1**, which must be broken on the way to the target, is an obvious complicating factor for its use as a starting material.

Previous approaches to monofunctionalize the symmetrical bicyclic octanedione unit **1** have employed multistep synthesis, whereas direct alkylation[6] or phenylsulfenylation reactions[7] met with only moderate success. In the majority of cases, prior to further elaboration, **1** has thus been converted to the monoketals **2**.[2-4,8] However, this involves protection-deprotection sequences accompanied by several recycle steps, with

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°) This paper is dedicated to Professor Paola Vita-Finzi on the occasion of her 60th birthday.

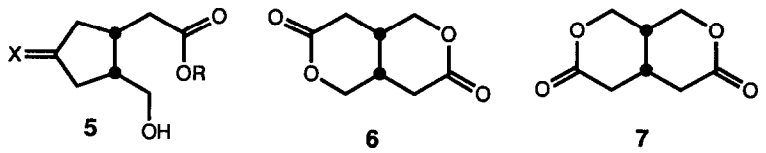
#) Part IV in the series: Synthetic Studies on Biologically Active Natural Compounds. For Part III see Garlaschelli, L.; De Tullio, P.; Vidari, G. *Tetrahedron* **1991**, *47*, 6759.

subsequent loss of overall yield. Moreover, the pure monoketal cannot be stored for long because it tends to disproportionate, hampering this approach. As a further limitation, compound **1** has been used so far only for the synthesis of molecular targets preserving the original diquinane structure. To expand the versatility of **1** in synthesis, we thought to modify the oxidation state of one of the two homotopic carbonyl groups without resorting to any protection and still preserving one cyclopentane ring. Keto-lactone **3**, in principle obtainable by a controlled Baeyer-Villiger oxidation of **1**, appeared, from a synthetic standpoint, to be endowed with several attractive features. In fact **3** contains three chemically very well differentiated oxygenated functions, among which the two versatile carbonyl groups offer potential for the regioselective introduction of substituents at the sp^2 carbon atom or at the adjacent positions. Importantly, the stereoselectivity of such reactions should be easily predictable under conditions of kinetic control, considering the different steric hindrance of the concave and convex sides of the *cis*-fused bicyclic structure of **3**. Furthermore, the chemical nature of the lactone function enables **3** to be considered as either a cyclopentane tetrahydropyran derivative or as a masked *cis*-1,2-disubstituted hydroxymethylcyclopentanecarboxylic acid ester **5**, thus paving the road to an array of selective transformations of the original molecule..

In this paper we describe our results on the synthesis of lactone **3** and its conversion to an advanced synthetic intermediate of Büchi's synthesis of loganin (**4**).

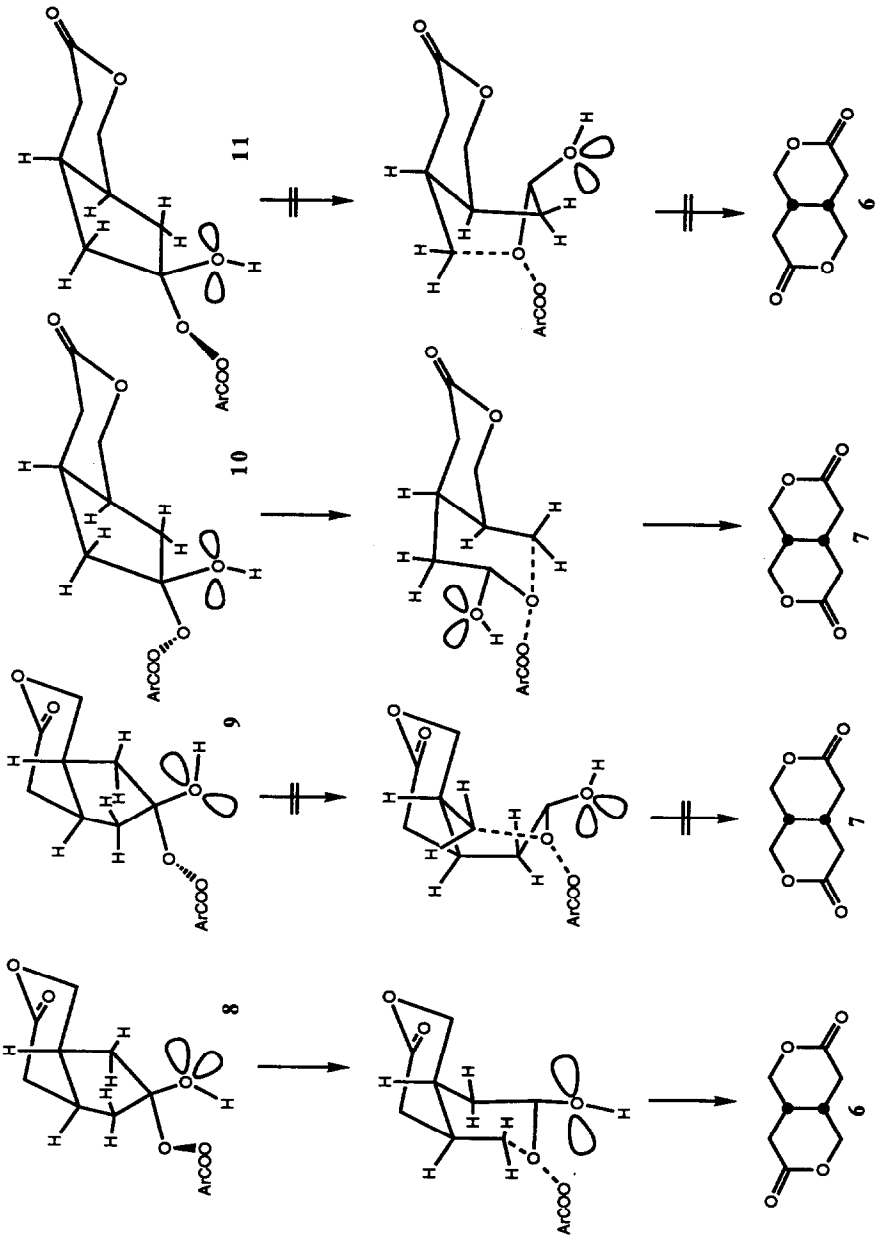
RESULTS AND DISCUSSION

Several reagents recommended for performing the Baeyer-Villiger oxidation of cyclopentanones were tested for oxidation efficiency of diketone **1** to compound **3**, while keeping the amount of overoxidation products **6** and **7** as low as possible.



The reaction was followed by GC analysis under conditions (see experimental part) where the starting material **1** and the products **3** and **6** (+7) are well separated peaks. On the contrary, on TLC plates, **3** and **6** (+7) have the same mobility using several different eluents and could not be separated .

With peroxymaleic acid, prepared *in situ*,[9] and with $(NH_4)_2Ce(NO_3)_6$ in MeCN-H_2O [10] extensive decomposition of products was observed, whereas using Na_2CO_4 in MeOH or CF_3COOH,[11] or with Mg-monoperphthalate in MeOH, [12] the reaction was too slow to be synthetically useful. Other reagents had to be discarded because of the high amount of bislactones **6** and **7** already formed even for a low conversion of starting material **1**. For example, with CF_3CO_2OH in CH_2Cl_2,[13] the ratio **1**:**3**:**6**(+**7**) was 50:35:15 at 0° C, while with oxone in the presence of "wet alumina" [14] the overoxidation of **3** was even faster, leading to a ratio of 3:16 after a conversion of only 20% **1**. Eventually MCPBA was the reagent of choice to achieve reasonable yields of ketolactone **3**. Under strictly controlled conditions of temperature, solvent and MCPBA concentration, oxidation of bicyclo[3.3.0]octane-3,7-dione afforded **3** and starting material **1** in a ratio ~ 4:3, in the presence of 8-10 % bislactones **6** and **7** (GC analysis). This result was considered the best compromise between driving the oxidation of diketone **1** to a greater extent and hindering its chromatographic separation for the presence of a larger amount of bislactones. After one recycle of recovered starting material **1**, **3** was obtained in 55-60 % isolated overall yield (64-70 % on recovered diketone **1**). The efficiency of the entire process, usually performed on a 2-20 g scale, is thus only moderate but it can be considered acceptable for giving direct access to the valuable synthon **3**. In an ultimate effort to improve the yields of the oxidative reaction, modified MCPBA reagents were tested, but they met with no real improvement. Oxidation of **1** with

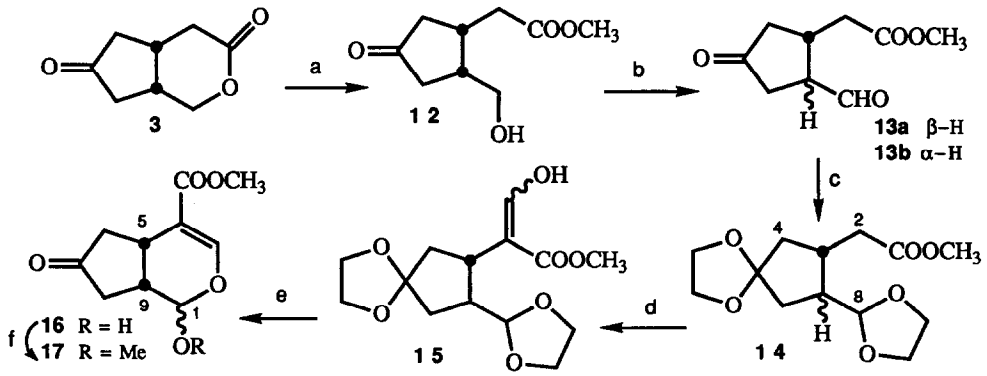


Scheme 1

Transition states for MCPBA oxidation of 3 to 6 and 7

MCPBA in the solid state,[15] in H_2O [16] or with added CF_3COOH to a CH_2Cl_2 solution[17] was much faster, however afforded an unfavorable ratio of monolactone **3** and bislactones **6** + **7**. In another set of experiments the Baeyer-Villiger reaction was carried out in several mixtures of CH_2Cl_2 and THF containing different amounts of the latter solvent. Although we were well aware of the dangerous formation of peroxides, we felt that THF could compete with lactone **3** as a substrate for the oxidation, thus depressing overoxidation of **3**. The reaction rate was indeed lowered with respect to the use of CH_2Cl_2 as a solvent alone (from few hours to several days), but with no significative improvement of the yields of ketolactone **3**.

Interestingly, oxidation of diketone **1** to completion with excess MCPBA afforded a non statistical mixture of bislactones **6** and **7** in 80% yield. The two compounds could not be separated by chromatography, however NMR spectroscopy allowed to assign the more abundant and the minor product structures **6** and **7**, respectively. In fact the broad band ^1H decoupled ^{13}C-NMR spectrum showed a total of nine well separated singlets whose multiplicity was established by DEPT and ^1H-^{13}C COSY experiments. The four signals showing a much higher intensity were assigned to compound **6** of C_2 symmetry, while the five isochronous singlets of lower intensity are consistent with structure **7** of C_S symmetry. Integration of the multiplets between δ 3.9-4.25 in the ^1H-NMR spectrum of the mixture allowed us to estimate the ratio between **6** and **7** as 4:1. As this result clearly depends on kinetic factors, a difference of $\Delta\Delta G^{\neq} \sim 3.5$ KJ mol $^{-1}$ must exist at room temperature between the activation energy of the two reactions leading to **6** and **7** respectively. Although various factors affecting the Baeyer-Villiger reaction are poorly understood, such a small gap of energy can be due to a combination of conformational, steric and stereoelectronic effects in the transition states. We assumed that the peracid reacts on the less hindered convex face of the carbonyl group of compound **3** and one of the non-bonded electron pairs of the hydroxyl group in the corresponding tetrahedral species is antiperiplanar to the migrating C-C bond, which in turn must be antiperiplanar to the ArCOO-O bond.[18] In principle, only four different conformations having the lactone ring in the favoured chair form [19] and the hydroxyl hydrogen turned outside the six membered ring can fulfil such stereoelectronic requirements (**8**, **9**, **10** and **11** in scheme 1). Transition states **9** and **11** are eliminated on the basis of the boat conformation of the incipient lactone ring. Also, conformation **10** leading to **7** should be less stable than conformation **8** affording **6**, because in the former the leaving ArCOO group is expelled along an axial trajectory, while in the latter it occupies an equatorial orientation. It is also possible that a coulombic repulsion between the dipoles associated with the two carbonyl groups, more pronounced in structure **7** than in **6**, is already developing in the transition states, thus disfavoring bislactone **7**.



Scheme 2

Reagents: a) MeONa; b) $(Cl_3CO)_2CO$, DMSO, Et_3N; c) $HOCH_2CH_2OH$, PTSA; d) LDA.THF complex, HCOOMe; e) aq. HCl-THF; f) MeOH, PTSA

To demonstrate the utility of ketolactone **3** as a building block for the synthesis of cyclopentanoid natural products, we prepared **17**, Büchi's intermediate [20] for loganin (**4**) synthesis (scheme 2). Opening of

the δ-lactone ring with MeONa/MeOH gave the δ-hydroxy methyl ester **12** which was immediately oxidized to aldehyde **13** by a modified Swern oxidation.[21] Crude **13** was contaminated by a small amount of lactone **3** for the great tendency of **12** to recyclize.

Aldehyde **13**, obtained in 76 % overall yield from **3** (91% on recovered **3**), was a mixture (~1:1) of the two formyl epimers, due to partial epimerization of the *cis* (**13a**) to the more stable *trans* 1,2-disubstituted cyclopentane derivative **13b**. However, this was of no further consequence for the stereochemical integrity of our synthetic target, because epimerization within the corresponding dialdehyde (*vide infra*) will lead to hemiacetal **16** with the more stable desired *cis* ring fusion.[20] Protection of the two carbonyl groups of **13a-b**, followed by formylation, deprotection and acid catalyzed ring closure gave **16**,[3a-b] as a mixture of epimeric hemiacetals. Brief exposure of the latter to MeOH and PTSA afforded a mixture of acetals (33% overall yield from **13**). Since the major β isomer of compound **17** has already been converted by Büchi into (±)-loganin (**4**),[20] this approach represents a formal synthesis of this widely distributed product of secondary plant metabolism.

We are currently engaged in further studies concerning the use of ketolactone **3** in synthesis and in obtaining this compound in enantiomerically pure form through asymmetric synthesis.

EXPERIMENTAL

Melting points were determined on a Fisher Johns hot plate and are uncorrected. IR spectra were recorded (film or KBr pellets) with a Perkin-Elmer model 257 spectrometer. ^{1}H- (300 MHz) and ^{13}C-NMR (75.47 MHz) spectra were recorded in $CDCl_3$ solution, using a Bruker CXP 300 spectrometer. Chemical shifts are reported in δ units with Me_4Si as internal standard; the abbreviations s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and b=broad are used throughout. Coupling constants (J) are reported in Hz. Mass spectra were determined with a Finnegan MAT 8222 instrument at 70 eV (0.5 mA) using a direct inlet system. Merck Kieselgel 60 (0.043-0.060 mm) were used for column chromatography. Analytical GF_{254} TLC plates (250 nm) were obtained from Merck. The spots were visualized under UV light or by spraying the plates with an EtOH sulphuric acid-vanillin solution and then heating at 120° C for few minutes. For GLC analysis a Perkin-Elmer Sigma 3B gas chromatograph with a FID and a WCOT CP-Sil-5CB, 1.09 μm film, 0.53 mm ID, 10 m column was used. The column temperature was increased from 70° to 250°C at 7°C/min, the carrier gas (N_2) flow rate was 11 cc/min, the injector temperature was 250°C and the detector temperature was 300°C. All solvents were purified and dried by standard techniques just before use. All reactions were routinely carried out under an inert atmosphere of dry, oxygen free, N_2 or argon. During work up of reactions, unless otherwise indicated, organic solutions were eventually washed with brine, then dried with $MgSO_4$ and filtered prior to rotary evaporation at water aspirator pressure. Residual solvent was removed under vacuum, usually at less than 1 torr. Reactions yields are for TLC and NMR homogeneous compounds. MCPBA was upgraded to ~99% assay by washing the commercially available (Aldrich) technical product (50-60%) with a phosphate buffer of pH 7.5 and drying the residue under reduced pressure.

Cis-3-oxabicyclo[4.3.0]-nonane-4,8-dione (**3**). Solid $NaHCO_3$ (1.53 g, 18 mmol) and then MCPBA (3 g, 17.4 mmol) in CH_2Cl_2 (100 mL) were added to diketone **1** (2.0 g, 14.5 mmol) in CH_2Cl_2 (150 mL) at 0°. The suspension was stirred at 7°C for ~ 23 h, until GC analysis showed the ratio of compound **1**:**3** to be ~ 3:4, in the presence of ~10% **6** and **7** (GC retention times: 3.31 min for **1**; 6.70 min for **3**; 9.69 min for the mixture **6** and **7**). After dilution with more CH_2Cl_2 (100 mL), solid $Na_2S_2O_5$ (25 g, 130 mmol) was added and the mixture was stirred overnight until reduction of excess peroxyacid, then it was filtered through a sintered-glass funnel washing thoroughly with CH_2Cl_2. The filtrate was taken to dryness and the residue was suspended in a small volume of CH_2Cl_2 (15 mL), filtered from undissolved *m*-chlorobenzoic acid and concentrated. After adding silica gel, the mixture was loaded over a silica gel column (200 g). Elution with hexane-AcOEt (1:1) afforded recovered diketone **1** (0.77 g); elution with hexane-AcOEt (1:4) gave in the

order ketolactone **3** (0.99 g, yield 44%) and a mixture of **6** and **7** (180 mg). Another MCPBA oxidation of the entire recovered starting material **1** under the same reaction conditions gave more ketolactone **3** (310 mg, 58 % overall yield), besides unreacted **1** (235 mg) and more **6** + **7** (86 mg).

3: mp 104°C (needles from AcOEt-Et_2O); IR (KBr) cm^{-1}: 1730 (CO),1481, 1432, 1395, 1291, 1260, 1186, 1148, 1129, 1056, 1022, 955, 819, 713; ^{1}HNMR, δ: 2.11 (1H, ddd, 19.0, 6.5 and 2.0, 7-H or 9-H), 2.18 (1H, ddd, 19.0, 6.0 and 2.0, 9-H or 7-H), 2.41 (1H, dd, 15.5 and 7.0, 5-H), 2.53 (1H, ddd, 19.0, 9.5, 2.0, 7'-H or 9'-H), 2.65 (1H, ddd, 19.0, 9.5 and 2.0, 9'-H or 7'-H), 2.8 (1H, dd, 15.5 and 7.0, 5'-H), 2.8-3 (2H, m, 6-H and 1-H), 4.12 (1H, dd, 12.0 and 7.5, 2-H), 4.39 (1H, dd, 12.0 and 5.0, 2'-H); ^{13}CNMR, δ_C: 215.3 (ketone CO), 171.7 (lactone CO), 69.5 (CH_2O), 44.0 (CH_2), 39.6 (CH_2), 32.4 (CH), 29.9 (CH); EIMS, *m/z* (% rel int.): 154 (M^+, 88), 126 (M - CO, 83), 113 (89), 82 (59), 71 (63), 68 (81), 67 (61), 54 (92), 42 (100), 41 (89).

^{1}HNMR of a mixture (4:1) of **6** + **7** , δ: 2.3-2.9 (6H, m), 3.9-4.10 (0.4 H, dd, 13.0 and 7.0), 4.10-4.25 (1.6H, dd, 13.0 and 7.0), 4.3-4.5 (2H, m); ^{13}CNMR of **6**, δ_C: 171.1 (CO), 68.8 (CH_2O), 29.9 (CH_2), 28.6 (CH); **7**, δ_C: 171 (CO), 66.2 (CH_2O), 33.7 (CH_2), 31.2 (CH), 26.4 (CH).

2-(2-Formyl-4-oxocyclopentyl)acetic acid methyl ester (**13**). To a solution of lactone **3** (300 mg, 1.94 mmol) in dry MeOH (18 mL) was added NaOMe (10.8 mg, 0.2 mmol) in MeOH (286 μL). After stirring overnight at room temperature, a saturated aq. NH_4Cl solution (0.5 mL) was added, and the solvent was evaporated under reduced pressure until a thick film was obtained. AcOEt (250 mL) and Celite (2 g) were added and the suspension filtered through a sintered-glass funnel. After removal of volatiles at reduced pressure under 40°C, **12** (350 mg) was obtained, pure enough for the oxidation step. IR (film) cm^{-1}: 3463 (OH), 2959, 1735 (CO), 1436, 1402, 1170, 1022; ^{1}HNMR, δ: 2.1-2.3 (2H, m), 2.3-2.5 (3H, m), 2.5-2.7 (2H, m), 2.8-3.0 (1H,m), 3.4-3.8 (2H, m, CH_2O), 3.7 (3H, s, OMe). To a stirred solution of bis(trichloromethyl)carbonate (328 mg, 1.1 mmol) in anhydrous CH_2Cl_2 (8 mL) at -78°C was added dry DMSO (470 μL, 6.6 mmol). The reaction mixture was stirred for 15 min and then a solution of compound **12** (328 mg, 1.76 mmol) in CH_2Cl_2 (3 mL) was slowly added at the same temperature. After stirring for 15 min at -78°C and 15 min at -60°C, NEt_3 (960 μL, 6.88 mmol) in CH_2Cl_2 was added dropwise, maintaining the temperature below -70°C. After the addition the resulting suspension was stirred at -78°C for 5 min and then at r. t. for 1 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 5% HCl (5 mL) and brine (5 mL). After drying and removal of solvents, benzene was added and the residual salts were filtered off through a Celite pad. The filtrate gave an oil which was chromatographed over silica gel. Elution with hexane-AcOEt in a 55:45 ratio afforded, besides recovered **3** (50 mg), 272 mg (76%) of ketoaldehydes **13a** and **13b** as a pale yellow oil; IR (film) cm^{-1}: 2956, 2736, (CHO), 1733 (CO), 1436, 1401, 1374, 1240, 1171, 1044, 997, 890; ^{1}HNMR, δ: 2.0-2.20 (1H, m), 2.35 (1H, bdd, 19.0, 8.5), 2.4-2.75 (4H, m), 2.85-3.0 (1H, m, 2-H and 6-H for one epimer), 3.0-3.15 (0.5 H, m, 2-H for the other epimer), 3.45-3.55 (0.5 H, m, 6-H for the other epimer), 3.70 and 3.71 (3H, two singlets, OMe), 9.75 and 9.95 (1 H, two doublets, 2.5 and 1.5 respectively, CHO); CIMS (isobutane) *m/z* (% rel. int.): 185 (M + H, 30), 155 (M - CHO, 17), 133 (30), 117 (38), 89 (35), 59 (78), 57 (100), 43 (65), 29 (6).

Bis-ethylene glycol ketals (*14*) *of ketoaldehydes* ***13a-b***. Ethylene glycol (100 μL, 1.78 mmol) was added to a solution of **13a-b** (55 mg, 0.3 mmol) and PTSA (3 mg) in dry benzene (3 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 4 h, then more benzene was added (25 mL) and washed with 5% aq. $NaHCO_3$ (5 mL). Chromatography of the crude product gave bis-ketals **14** (66 mg, 82%) as a colorless oil; IR (film) cm^{-1}: 2956, 2891, 1733 (ester CO), 1433, 1328, 1160, 1078, 1020, 947, 886; ^{1}HNMR, δ: 1.5-2.9 (8H, m, 2-H, 3-H, 4-H, 6-H, 7-H), 3.63 and 3.64 (3H, two singlets, OMe), 3.77-3.97 (8H, m, -OCH_2CH_2O-), 4.80 and 4.82 (1 H, two doublets, 5.5 and 5.5 respectively, 8-H); EIMS, *m/z* (% rel. int.): 272 (M^+, 9), 241 (M - OMe, 30), 227 (29), 199 (78), 171 (42), 139 (30), 125 (22), 113 (20), 100 (64), 86 (75), 73 (100), 45 (41), 41 (26).

Formylation of 14 and acid catalyzed cyclization to acetals 17. 1.5 M LDA.THF complex (Fluka) in cyclohexane (473 μL, 0.71 mmol) was added dropwise to a solution of ketals **14** (38 mg, 0.142 mmol) in THF (2 mL) at -78°C. The mixture was stirred for 30 min at -78°C and brought to r.t. in 3 min. After cooling again to -78°C methyl formate (175 μL, 2.86 mmol) was added dropwise. The solution was stirred for 30 min at -78°C, then at r.t. for 2 h and quenched with 5% aq. HCl. After work up the crude formylation product was dissolved in THF-5% HCl (3 mL, 1:1) and stirred for 20 h. After addition of brine, the water layer was extracted with CH_2Cl_2 (5 x 20 mL). The residue was chromatographed over silica gel (hexane-AcOEt 3:2), yielding **16** (12 mg) as a C-1 epimeric mixture (~1:1); IR (film) cm^{-1}: 3393 (OH), 1734 (cyclopentanone CO), 1705 (ester CO), 1631 (C=C), 1437, 1298, 1175, 1150, 1095, 1066, 905; ^{1}HNMR, δ: 2.15-2.8 (5H, m), 3.2 (bq, 8) and 3.3 (bq, 7) (together 1H, 5-H), two almost coincident singlets at 3.71 (3H, OMe), 5.15 (d, 6.0) and 5.50 (d, 3.2) (together 1H, 1-H), 7.48 (d, 1.5) and 7.50 (d, 1.5) (together 1H, 3-H); EIMS, *m/z* (% rel. int.): 212 (M^+, 33), 194 (14), 180 (14), 162 (19), 155 (37), 128 (41), 123 (100), 102 (15), 97 (25), 96 (80), 95 (20), 84 (24), 82 (22), 68 (38), 57 (71), 55 (26), 43 (22), 41 (28). The IR and ^{1}HNMR signals agree with those reported for **16** obtained from dione **1** by a completely different route.[3b] Lactols **16** were stirred overnight at r.t. in dry MeOH (10 mL) containing PTSA (2 mg). NaOMe was added and the solution was stirred for 4 additional hours, neutralized with AcOH and the product was isolated with AcOEt. The ^{1}HNMR spectrum of the crude mixture (10 mg) showed the same signals reported for acetals **17**.[20]

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