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Intramolecular Diels-Alder Reaction of Chiral, Highly Oxygenated Trienoates Derived from Sugar Allyltins

Sławomir Jarosz*, Elżbieta Kozłowska and (in part) Artur Jeżewski

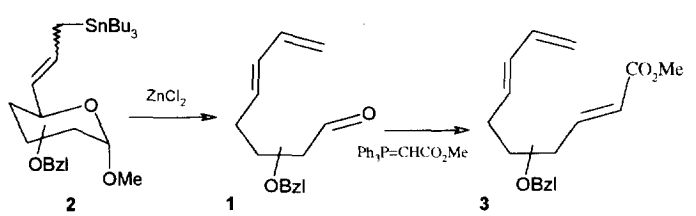
Institute of Organic Chemistry, Polish Academy of Sciences
Kasprzaka 44, 01-224 Warszawa (e-mail: SLJAR@ICHF.EDU.PL)

Abstract: *The Lewis acid catalyzed intramolecular Diels-Alder reaction of sugar derived trienoates* **3** *led preferably to bicyclic endo-adducts* **4**. *The best stereoselectivity was observed for cyclization of the L-arabino-trienoate* **3b**, *in which only one isomer (trans) was formed. High pressure (15 kbar) cycloaddition of* **3a**, **3b**, *and* **3c**, *led to single stereoisomers* **4a**, **4b**, *and* **4c** *in good yields. Conversion of adduct* **4a** *to chiral cyclopentanes was described.* © 1997 Elsevier Science Ltd.

INTRODUCTION

Diels-Alder reaction is one of the most important processes in the creation of the carbon-carbon bonds[1]. Intramolecular version of this reaction opens a convenient route to bicyclic products[2]; application of chiral precursors allows the synthesis of enantiomerically pure bicyclic adducts.

Recently[3] we proposed a convenient method for the preparation of chiral, highly oxygenated dienoaldehydes (**1**) from readily available sugar allyltin derivatives **2**. Treatment of **2** [with a D-*gluco*- (**a**), D-*galacto*- (**b**) and D-*manno*- (**c**), configurations] with a mild Lewis acid caused a rearrangement with elimination of tributyltin moiety and formation of chiral aldehydes **1** in high yield. These compounds were further converted[3] into trienoates **3a** (D-*xylo*-configuration), **3b** (L-*arabino*-), and **3c** (D-*lyxo*-) by reaction with (methoxycarbonyl)methylenetriphenylphosphorane. In this paper an intramolecular Diels-Alder reaction of trienes **3** leading to chiral bicyclo[4,3,0]non-2-enes (**4**) will be presented.



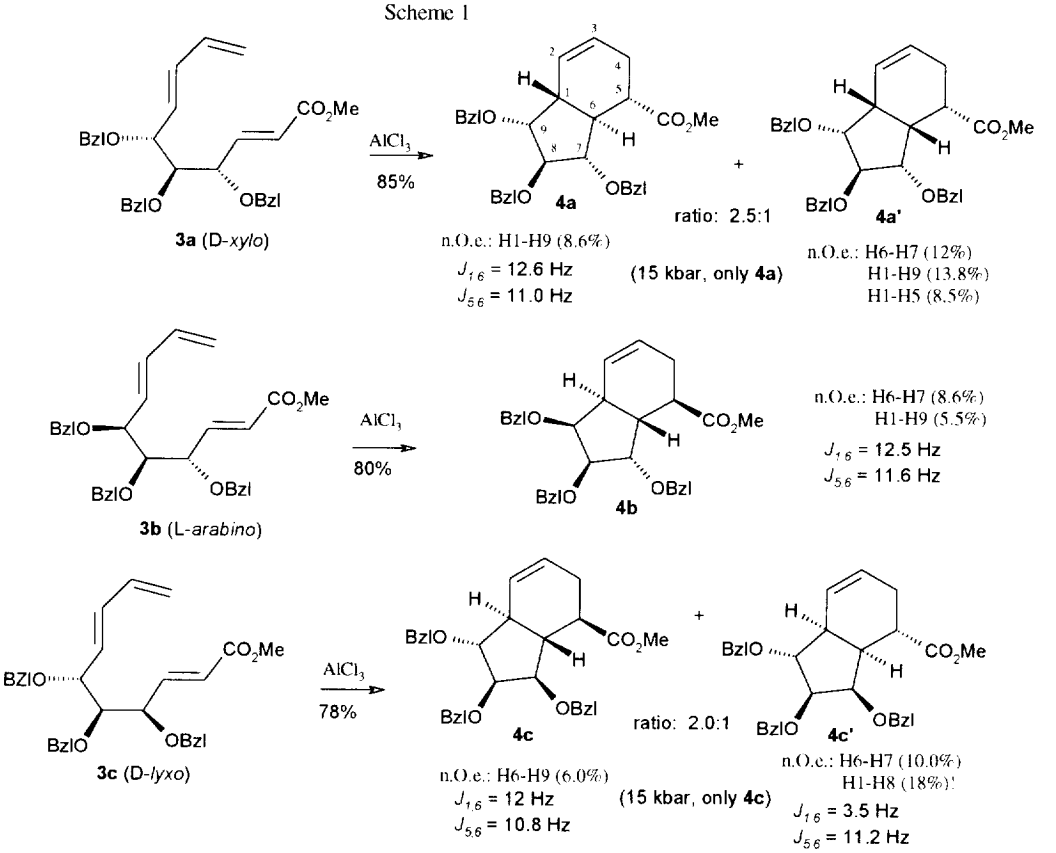
2 **1** **3**

RESULTS AND DISCUSSION

Treatment of trienoates **3** with a Lewis acid ($AlCl_3$) induced a smooth cyclization to bicyclic adducts **4** in 78-85% yield (see Scheme 1).

Cyclization of the D-*xylo*-triene **3a** (derived from *gluco*-allyltin) afforded two well separable products **4a'** and **4a** in a ratio 2.5:1. Cyclization of **3b** gave carbocyclic derivative **4b** as a single product, while **3c** under

Scheme 1



the same conditions furnished a 2:1 mixture of **4c** and **4c'**.

Structure of compounds **4** was established by careful NMR experiments: COSY (^1H-^1H and ^1H-^{13}C) and nuclear Overhauser effect (n.O.e); the most important n.O.e. values are listed in Scheme 1. Since the configuration of the cyclopentane ring at C7,8,9 in compounds **4** is known, the *cis*-relation of protons H1-H9 can be assigned from n.O.e.'s effects for **4a** (8.6%), **4a'** (13.8%) and **4b** (5.5%). Similarly, H6 and H7 in **4a'** and **4c'** are also in *cis*-arrangement (n.O.e. 12% and 10% respectively). Extremely high enhancement (18%) was observed between H1 and H8 in **4c'**. These assignments were additionally supported by ^1J coupling

constants in the six-membered ring between protons at the three newly created chiral centers (at C1, C5, and C6 positions); *trans*-arrangement between H1-H6 and H5-H6 can be deduced for **4a**, **4b**, and **4c** from the large coupling constants $J_{5,6}$ and $J_{1,6}$ although the 6-membered ring in **4** is distorted (see Scheme 1; unusually large values of coupling constants are probably caused by a distortion arising from the presence of a double bond and a fused 5-membered ring). Similar values of these constant were found in saturated diacetate **6** (see Scheme 2) suggesting that distortion of **4** arising from the presence of a double bond has little effect on this parameter.

As expected the *endo*-adducts were formed preferably (**4a**, **4c**) or exclusively (**4b**); appropriate stereochemical models of the *endo* transition states (leading to **4a**, **4b** and **4c**) are presented in Fig. 1.

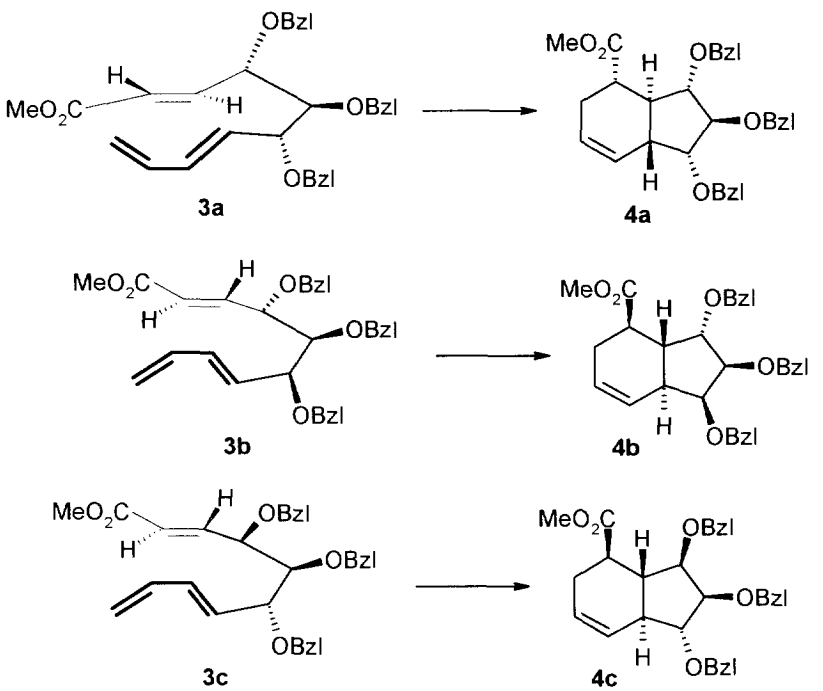


Fig. 1. Stereochemical models for intramolecular *endo*-cyclizations of trienes **3a-c**.

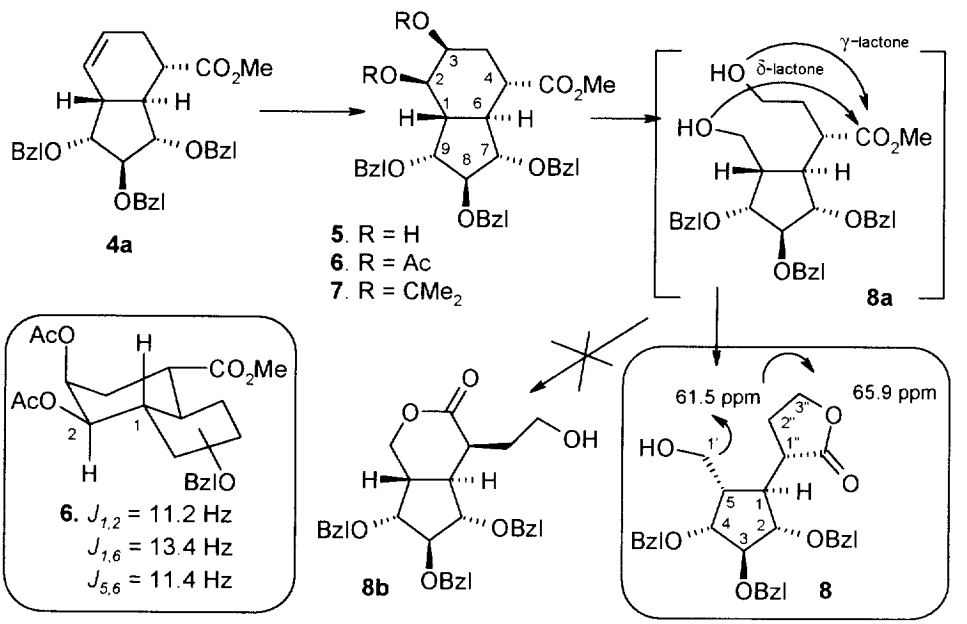
It is known that Diels-Alder reactions are accelerated under high pressure[4] and often better selectivities are achieved. We applied this technique (15 kbar at 50°C; no catalyst) to our problem and found that [4+2] cycloaddition of trienes **3** led exclusively to *endo* products (**4a**, **4b**, and **4c**) in good yields; no other stereoisomers were seen.

Compounds **4** can be useful synthons for the preparation of highly functionalized cyclohexane and cyclopentane derivatives what is illustrated in Scheme 2 for compound **4a**.

Catalytic osmylation[5] of **4a** led to a single product - diol **5**. Configuration of this product was assigned from the ^{1}H NMR spectrum of its diacetate **6**; coupling constant $J_{1,2}$ = 11.4 Hz clearly pointed at the *trans*

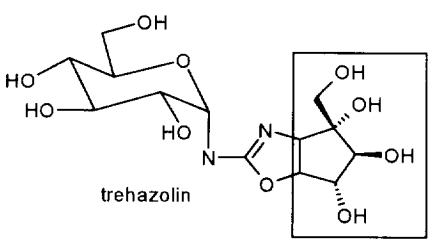
arrangement of protons H1 and H2 in the 6-membered ring (see Scheme 2). The large value of $J_{5,6}$ and $J_{1,6}$ (11.9 and 13.4 Hz respectively) indicated also the *trans*-relations of protons H1-H6 and H5-H6 in the six-membered (not distorted as **4a**) ring thus, giving additional support for structure **4a**.

Scheme 2



Action of dimethoxypropane on diol **5** afforded another cyclohexane derivative (**7**) in good yield.

Highly oxidized cyclopentane derivatives possess interesting biological properties. For example trehazolin is strong inhibitor of trehalaze[6]. Other compounds of this type are also components of antiviral antibiotics[7]. Similarly, carbocyclic analogs of nucleosides[8] may be used for study of biological processes.



We explored the possibility of conversion of bicyclic Diels-Alder adducts obtained from trienes **3** into chiral, highly oxygenated cyclopentanes what is shown in Scheme 2 (for compound **4a**).

Periodic cleavage of diol **5** (obtained from **4a**) followed by sodium borohydride reduction (→ **8a**) and *in situ* lactonization afforded γ-lactone **8**. The alternative cyclopentane derivative (δ-lactone **8b**) was excluded on the basis of the ^{13}C NMR spectrum: signal of the -C(1')H_2O- group attached to a cyclopentane ring resonated at higher field (C-1': δ 61.5 ppm) than the one observed for -C(3'')H_2O- (C-1'': δ 65.9 ppm) thus, suggesting that the C3''-OH group was involved in formation of a lactone.

In conclusion, aluminum chloride catalyzed intramolecular [4+2] cycloaddition of trienes **3** - derived from sugar allyltins readily available in our laboratory - gave bicyclic adducts **4** in good chemical yield,

although with moderate (except for **3b**) stereoselectivity. Application of high pressure for this [4+2] intramolecular cyclization reaction improved dramatically the steric course of this process; only the *endo* adducts were formed in good yields.

The bicyclic adducts can be converted into chiral, highly oxidized cyclopentanes as was illustrated by transformation of **4a** into **8**.

Acknowledgment: This work was supported by a Grant **2P303 038 07** from the State Committee for Scientific Research, which is gratefully acknowledged.

Experimental

General methods: NMR spectra were recorded with a Bruker AM 500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. All resonances were assigned by COSY (^1H-^1H and ^1H-^{13}C) correlations. Mass spectra [LSIMS (m-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added) or EI] were recorded with a AMD-604 (AMD Intectra GmbH, Germany) mass spectrometer. Specific rotations were measured with a JASCO DIP Digital Polarimeter for chloroform solution (c~1) at room temperature. Column chromatography was performed on silica gel (Merck, 70-230 mesh). Organic solutions were dried over anhydrous magnesium sulfate.

General procedure for intramolecular [4+2] cyclization of trienes 3

a. catalyzed with aluminum chloride. To a solution of triene **3** (*ca* 0.5 mmol) in toluene - ether (95:5, 10 mL) freshly sublimed aluminum chloride (5 mg) was added and the mixture was stirred at room temperature for 1 h. Water (2 mL) was added, the organic layer was separated, dried and concentrated and the product(s) was isolated by column chromatography (hexane - ethyl acetate, 9:1 to 7:1). Cyclization of **3a** gave **4a'** (24%) and **4a** (59%); cyclization of **3b** afforded single stereoisomer **4b** (80%); cyclization of **4c** led to **4c'** (26%) and **4c** (53%).

b. under high pressure (the high-pressure reactions were performed in a piston-cylinder type apparatus according to ref. 9). A solution of **3** (*ca* 10 mg) in toluene (2 mL) was kept at 50°C under 15 kbar pressure for 24 h and products **4** were isolated (as above) by column chromatography; yields: **4a** - 78%, **4b** - 70% (+ 15% of recovered starting material), and **4c** - 80%.

*1(R),5(S),6(S),7(S),8(S),9(R)-7,8,9-Tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]non-2-ene (minor isomer **4a'**).* $[\alpha]_D$ -38.2°; ^1H NMR δ: 5.94 ($J_{2,3}$ 9.6 Hz, H-2), 5.60 ($J_{3,4}$ 4.2 and 2.7 Hz, H-3), 3.95 ($J_{8,9}$ 3.7, $J_{7,8}$ 6.4 Hz, H-8), 3.94 ($J_{6,7}$ 4.6 Hz, H-7), 3.64 ($J_{1,9}$ 9.9 Hz, H-9), 3.62 (s, OCH_3), 3.01 ($J_{4,5}$ 6.5, $J_{5,6}$ 11.3 Hz, H-5), 2.74 (H-1), 2.48 and 2.20 (2m, H-4,4'), 1.99 (m, H-6); n.O.e. values: H6-H7 (12%), H1-H9 (13.8), H5-

H1 (8.5), H1-H7 (6.0); ^{13}C NMR δ: 175.3 (COOMe), 128.0 (C-2), 126.2 (C-3), 89.9 (C-8), 88.6 (C-9), 81.0 (C-7), 51.5 (OCH_3), 43.5 (C-6), 43.3 (C-1), 39.6 (C-5), 30.0 (C-4); HR-MS calc for $C_{32}H_{34}O_5Na$ ($M + Na^+$): 521.2304. Found: 521.2304.

*1(R),5(S),6(R),7(S),8(S),9(R)-7,8,9-Tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]non-2-ene (major isomer **4a**).* $[\alpha]_D$ +18.9°; ^{1}H NMR (C_6D_6) δ: 5.81 (dd, $J_{2,3}$ 9.9, $J_{1,2}$ 1.9 Hz, H-2), 5.54 (dd, $J_{3,4}$ 2.7, $J_{3,4}$ 4.6 Hz, H-3), 3.95 ($J_{7,8}$ 3.1 Hz, H-8), 3.92 (H-7), 3.66 ($J_{1,9} = J_{8,9}$ 4.5 Hz, H-9), 3.36 (s, OCH_3), 2.81 ($J_{6,7}$ 9.6 Hz, H-6), 2.66 (H-4), 2.57 ($J_{5,4}$ 5.3, $J_{5,6}$ 11.0 Hz, H-5), 2.23 ($J_{1,6}$ 12.6 Hz, H-1), 2.11 (m, H-4'); n.O.e. values: H1-H9 (8.6%); ^{13}C NMR δ: 175.31 (COOMe), 127.4 (C-3), 125.6 (C-2), 89.5 (C-8), 88.8 (C-7), 80.9 (C-9), 50.9 (OCH_3), 45.1 (C-6), 44.7 (C-1), 43.9 (C-5), 29.1 (C-4); HR-MS calc for $C_{32}H_{34}O_5Na$ ($M + Na^+$): 521.2304. Found: 521.2310.

*1(S),5(R),6(S),7(S),8(S),9(S)-7,8,9-Tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]non-2-ene (**4b**).* $[\alpha]_D$ -21.1°; ^{1}H NMR: 5.85 (dd, $J_{2,3}$ 9.9, $J_{1,2}$ 2.1 Hz, H-2), 5.61 (dd, $J_{3,4}$ 7.1 Hz, H-3), 4.10 ($J_{8,9}$ 4.7, $J_{1,9}$ 3.3 Hz, H-9), 4.06 ($J_{7,8}$ 2.1, $J_{6,7}$ 6.6 Hz, H-7), 3.86 (dd, $J_{8,9}$ 4.7, $J_{7,8}$ 2.2 Hz, H-8), 2.85 ($J_{4,5}$ 6.0, $J_{5,6}$ 11,5 Hz, H-5), 2.63 ($J_{6,7}$ 6.6, $J_{1,6}$ 12.5 Hz, H-6), 2.43 ($J_{4,5}$ 6.4 Hz, H-4), 2.39 (m, H-1), 2.20 (m, H-4'); n.O.e. values: H6-H7 (8.6%), H1-H9 (5.5%); ^{13}C NMR δ: 175.4 (COOMe), 127.4 (C-3), 126.8 (C-2), 88.7 (C-8), 82.7 (C-7), 77.8 (C-9), 51.3 (OCH_3), 43.8 (C-1), 42.6 (C-6), 40.3 (C-5), 30.0 (C-4); HR-MS calc for $C_{32}H_{34}O_5Na$ ($M + Na^+$): 521.2304. Found: 521.2299.

*1(S),5(R),6(S),7(R),8(S),9(R)-7,8,9-Tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]non-2-ene (minor isomer **4c'**).* $[\alpha]_D$ +32.9°; ^{1}H NMR δ: 5.90 (d, $J_{2,3}$ 9.9 Hz, H-2), 5.63 ($J_{3,4}$ 4.3 Hz, H-3), 4.26 (t, $J_{7,8}$ 4.2, $J_{6,7}$ 4.0 Hz, H-7), 4.00 (dd, $J_{8,9}$ 1.8 Hz, H-8), 3.98 (dd, $J_{1,9}$ 6.5 Hz, H-9), 3.63 (s, OCH_3), 2.98 (ddd, $J_{4,5}$ 6.5 and 11.3, $J_{5,6}$ 11.3 Hz, H-5), 2.86 (m, H-1), 2.48 (m, H-4), 2.25 (m, H-4'), 2.18 (m, $J_{1,6}$ 3.5 Hz, H-6); n.O.e. values: H6-H7 (10.0%), H1-H8 (18.0), ^{13}C NMR δ: 175.6 (COOMe), 126.7 (C-2), 126.1 (C-3), 88.9 (C-8), 82.6 (C-9), 77.8 (C-7), 51.5 (OCH_3), 43.7 (C-6), 42.3 (C-1), 40.1 (C-5), 29.7 (C-4); HR-MS calc for $C_{32}H_{34}O_5Na$ ($M + Na^+$): 521.2304. Found: 521.2304.

*1(S),5(R),6(R),7(R),8(S),9(R)-7,8,9-Tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]non-3-ene (major isomer **4c**).* $[\alpha]_D$ +66.3°; ^{1}H NMR δ: 5.91 (ddd, $J_{2,3}$ 9.9, $J_{1,2}$ 1 Hz, H-2), 5.64 ($J_{3,4}$ 4.3 Hz, H-3), 3.98 (dd, $J_{7,8}$ 6.6, $J_{8,9}$ 2.7 Hz, H-8), 3.75 (dd, $J_{6,7}$ 10.7 Hz, H-7), 3.72 (dd, $J_{1,9}$ 9.5 Hz, H-9), 3.49 (s, OCH_3), 2.61 (dt, $J_{4,5}$ 6.1 and 10.8, $J_{5,6}$ 10.8 Hz, H-5), 2.46 and 2.31 (2m, both H-4), 2.23 (m, $J_{1,6}$ 12 Hz, H-6), 2.11 (m, H-1); n.O.e. values: H6-H9 (6.0%); ^{13}C NMR (C_6D_6) δ: 174.4 (COOMe), 126.7 (C-2), 126.1 (C-3), 87.4 (C-9), 82.0 (C-8), 81.4 (C-7), 51.2 (OCH_3), 45.7 (C-6), 44.8 (C-5), 43.8 (C-1), 29.5 (C-4); HR-MS calc for $C_{32}H_{34}O_5Na$ ($M + Na^+$): 521.2304. Found: 521.2304.

*Cis-Hydroxylation of **4a**.* The general procedure for catalytic osmylation[5] was followed; thus, compound **4a** (210 mg, 0.42 mmol) in THF (4 mL) containing *tert*-BuOH (0.3 mL) and water (0.03 mL) was treated with osmium tetraoxide (0.2 mL of a ~2% solution in *t*-BuOH) and N-methylmorpholine-N-oxide (66 mg) for 24 h

at room temperature. Methanol (5 mL) was added and the oxidant was decomposed by addition of 40% aq. $NaHSO_3$ solution. After stirring for 30 min inorganic salts were filtered off, the filtrate concentrated and a crude product was extracted with ether. Column chromatography (hexane - ethyl acetate, 1:1) afforded single stereoisomer **5** (212 mg, 0.40 mmol, 95%). $[\alpha]_D$ +59.6°, HR-MS calc for $C_{32}H_{37}O_7$ ($M + H^+$): 533.2539. Found: 533.2540. This compound was fully characterized as diacetate **6** (87% yield).

1(R),2(S),3(S))5(S),6(R),7(S),8(S),9(R)-2,3-Di-O-acetyl-7,8,9-tri-benzyloxy-5-methoxycarbonyl-bicyclo[4,3,0]nonane (**6**): $[\alpha]_D$ +75.7°, ^{1}H NMR: 5.53 ($J_{2,3}$ 2.8, $J_{3,4'}$ 2.3, $J_{3,4}$ 5.8 Hz, H-3), 5.16 (dd, $J_{1,2}$ 11.4, $J_{2,3}$ 3.0 Hz, H-2), 3.87-3.82 (m, H-8 and H-7), 3.72 ($J_{1,9}$ 4.2 Hz, H-9), 3.50 (s, OCH_3), 2.58 (dt, $J_{4,5}$ 3.6, $J_{4,5'} = J_{5,6}$ 11.9 Hz, H-5), 2.39 (ddd, $J_{6,7}$ 8.8, $J_{1,6}$ 13.4, $J_{5,6}$ 11.4 Hz, H-6), 2.16 (ddd, 1H, $J_{1,9}$ 4.3, $J_{1,6}$ 13.4 Hz, H-1), 2.04 (s, CH_3), 2.02 (m, H-3) 1.92 (m, H-3'), 1.88 (s, CH_3); ^{13}C NMR: 174.1 and 170.0 (both acetates), 89.8 and 87.5 (C-7,8), 77.9 (C-9), 70.2 (C-2), 68.5 (C-3), 51.7 (OCH_3), 46.2 (C-6), 42.3 (C-5), 42.2 (C-1), 32.4 (C-4), 21.0 and 20.9 (2 x CH_3); HR-MS calc for $C_{36}H_{40}O_9Na$ ($M + Na^+$): 639.2566. Found: 639.2570.

1(R),2(S),3(S),5(S),6(R),7(S),8(S),9(R)-7,8,9-Tri-benzyloxy-2,3-O-isopropylidene-5-methoxycarbonyl-bicyclo[4,3,0]nonane (**7**): To a solution of **5** (186 mg, 0.35 mmol) in acetone (15 mL) containing catalytic amount (~5 mg) of *p*-toluenesulfonic acid, dimethoxypropane (0.2 mL) was added and the mixture was stirred for 15 min at room temperature. Triethylamine (0.1 mL) was added, the solvent was evaporated to dryness and the crude product was purified by column chromatography (hexane - ethyl acetate, 4:1 to 3:1) to yield acetonide **7** as an oil (175 mg, 0.31 mmol, 87%). $[\alpha]_D$ +50.8°; ^{1}H NMR: 4.46 (dd, $J_{2,3}$ 9.2, $J_{1,2}$ 4.6 Hz, H-2), 4.34 (dd, $J_{3,4}$ 2.2, $J_{2,3}$ 3.0 Hz, H-3), 3.91 (d, $J_{8,9}$ 4.6 Hz, H-9), 3.85 (d, $J_{7,8}$ 3.4 Hz, H-8), 3.77 (dd, $J_{6,7}$ 8.9 Hz, H-7), 3.48 (s, OCH_3), 2.56 (td, $J_{4,5}$ 3.9, $J_{4',5} = J_{5,6}$ 11.9 Hz, H-5), 2.30 (ddd, $J_{3,4}$ 2.2, $J_{4,4'}$ 15.3, $J_{4,5}$ 3.8 Hz, H-4), 2.07 (ddd, $J_{5,6}$ 11.1, $J_{1,6}$ 13.9 Hz, H-6), 2.00 (ddd, $J_{4',5}$ 12.3, $J_{3,4'}$ 4.0 Hz, H-4'), 1.82 (ddd, $J_{1,9}$ 9.4, $J_{1,2}$ 4.6 Hz, H-1), 1.49 (s, CH_3), 1.36 (s, CH_3). HR-MS calc for $C_{35}H_{41}O_7$ ((M + H$^+$): 573.2852. Found: 573.2848

1(S)-Hydroxymethyl-2(R),3(R),4(S)-tri-O-benzyl-5(S)-[1''(S)-tetrahydrofuran-3-one] (***8***). To a suspension of silica gel (Merck; 230-400 mesh, 193 mg) in methylene chloride (1.5 mL) a solution of sodium *m*-periodate (27 mg, 0.125 mmol) in water (0.2 mL) was added and the mixture was stirred at room temperature. After 20 min a solution of diol **5** (51.9 mg, 0.098 mmol) in methylene chloride (2 mL) was added and stirring was continued for another 3 h. The solid was filtered off, the solvent evaporated to dryness, and a residue was treated under standard conditions (in THF - MeOH, 4:1) with sodium borohydride (4 mg) for 40 min. Crude product was purified by column chromatography (hexane - ethyl acetate, 2:1 to 1:1) to yield lactone **8** as an oil (45 mg, 0.09 mmol, 91%); $[\alpha]_D$ +1.5°; ^{1}H NMR (C_6D_6): 4.00 (dd, $J_{2,3}$ 3.9, $J_{3,4}$ 3.4 Hz, H-3), 3.92 (dd, $J_{2,3}$ 3.9, $J_{1,2}$ 8.4 Hz, H-2), 3.88 (dd, $J_{3,4}$ 3.1, $J_{4,5}$ 6.2 Hz, H-4), 3.79 (2 H, $J_{1',5}$ 5,0 Hz, both H-1'), 3.60 and 3.31 (both H-3''), 2.79 (ddd, $J_{1,1'}$ 4.4, $J_{1,2}$ 8.6, $J_{1,5}$ 10.3 Hz, H-1), 2.39 (dt, $J_{1'',1}$ 4.4, $J_{1'',2''}$ 9.4 Hz, H-1''), 2.35 (td, $J_{1',5'}$ 5.1, $J_{5,1}$ 11.0 Hz, H-5) 1.75 (ddd, $J_{2'',3''}$ 8.8, $J_{1'',2''}$ 12.5 Hz, H-2''), 1.30 ($J_{2'',3''}$ 3.6, $J_{2'',3''}$ 7.2, $J_{3'',1''}$ 9.3 Hz, H-2''); ^{13}C NMR: 178.7 (C=O), 87.6 (C-3), 86.2 (C-2), 83.7 (C-4), 65.9 (C-3''), 61.5 (C-

1'), 43.8 (C-5), 43.2 (C-1), 39.5 (C-1''), 26.0 (C-2''). HR-MS calc for $C_{31}H_{35}O_6$ ($M + H^+$): 503.2222. Found: 503.2219.

REFERENCES

1. Pindur, U.; Lutz, G.; Otto, Ch. *Chem. Rev.*, **1993**, *93*, 741.
2. *a.* Fraser-Reid, B.; Benko, Z.; Guiliano, R.; Sun, K.M.; Taylor, N. *J. Chem. Soc., Chem. Comm.*, **1984**, 1029; *b.* Roush, W.R., *Advances in Cycloaddition,* **1990**, *2*, 91 and references therein; *c.* Herczegh, P.; Zsely, M.; Szilagyi, L.; Bajza, I.; Kovacs, A.; Batta, G., Bognar, R. *Cycloaddition Reactions in Organic Chemistry*, **1992**, 112 (ACS Symposium Series *494*, Guiliano R.M. Edition); *d.* Ishikara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.*, **1996**, *118*, 3049; *e.* Ainsworth, P.J.; Craig, D.; Reader, J.C.; Slawin, A.M.Z.; White, A.J.P.; Williams, D.J. *Tetrahedron,* **1996**, *52*, 695; *f.* Ainsworth, P.J.; Craig, D.; White, A.J.P.; Williams, D.J. *Tetrahedron,* **1996**, *52*, 8937; *g.* Deagostino, A.; Maddaluno, J.; Prandi, C.; Venturello, P. *J. Org. Chem.*, **1996**, *61*, 7597; *h.* Gwaltney II, S.L.; Sakata, S.T.; Shea, K.J. *J. Org. Chem.*, **1996**, *61*, 7438.
3. Kozłowska, E.; Jarosz, S. *J. Carbohydr. Chem.*, **1994**, *13*, 889.
4. Jenner, G. *Tetrahedron,* **1997**, *53*, 2669.
5. Van Rheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.*, **1976**, *17*, 1973; Jarosz, S. *Carbohydr. Res.*, **1992**, *224*, 73.
6. Ando, O.; Satake, H.; Itoi, K.; Sato, A.; Nakajima, M.; Takahashi, S.; Haruyama, H. *J. Antibiot.*, **1991**, *44*, 1165; Kobayashi, Y.; Miyazaki, H.; Shiozaki, M. *J. Am. Chem. Soc.*, **1992**, *114*, 10065.
7. Helmuchen, G.; Krotz, A.; Neumann, H.-P.; Ziegler, M.L., *Liebigs Ann.*, **1993**, 1313; Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.*, **1993**, *34*, 1313; Yoshikawa, M.; Yokokawa, Y.; Inoue, Y.; Yamaguchi, S.; Murakami, N. *Tetrahedron*, **1994**, *50*, 9961.
8. Agrofoglio, L.; Suhas, E.; Farese, A.; Condom, R.; Challand, S.R.; Earl, R.A.; Guedj, R. *Tetrahedron*, **1994**, *50*, 10611; Takahashi, S.; Inoue, H.; Kuzuhara, H. *J. Carbohydr. Chem.*, **1995**, *14*, 273.
9. Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis*, **1979**, 41; Jurczak, J.; Gryko, T.D. *in "Chemistry under Extreme or Non-Classical Conditions"*, **1997**, chapter 4 (van Eldik, R. and Hubbard, C.D. Ed., Wiley & Son s, Inc. and Spektrum Akademischer Verlag Co-Publication).

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