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TETRAHEDRON: *ASYMMETRY*

A convenient route to enantiomerically pure highly oxygenated decalins from sugar allyltin derivatives[1]

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Abstract

Preparation of enantiomerically pure, highly oxygenated decalins via tandem Wittig-type Diels–Alder reactions from the corresponding sugar-derived dieno-phosphoranes and/or -phosphonates and sugar aldehydes is described. Application of the phosphonates is more convenient than phosphoranes since the former can be prepared in much higher yields and react with aldehydes under milder conditions. The intermediate trienes resulting from the Wittig-type process undergo spontaneous and highly stereoselective cyclization to the *cis*-decalins under the reaction conditions.

1. Introduction

Transformation of simple monosaccharides into enantiomerically pure carbocyclic compounds (the 'chiron' approach[2]) is now one of the most convenient methods for the preparation of highly oxygenated cyclopentane[3] and cyclohexane[4] derivatives. Synthesis of more complex enantiomerically pure carbobicyclic derivatives can be achieved also by this methodology.[5,6]

The main task in such an approach to enantiomerically pure carbocyclic system from carbohydrates (probably one of the most useful and simplest methodologies) is the preparation of appropriate sugar-derived reagents–chirons.

Recently, we elaborated a convenient method of the synthesis of chiral dienoaldehydes **1** from sugar allyltins **2**.[7] Such aldehydes were used for the preparation of chiral cyclopentane derivatives[8] **3** and — after conversion into trienes **4** (by reaction with appropriate Wittig or Wittig–Horner reagents) — into enantiomerically pure highly oxygenated bicyclo[4.3.0]nonane derivatives[9] **5** (Fig. 1).

The readily available dienoaldehydes **1** may serve also as synthons for chiral decalin derivatives such as **6**. This carbocyclic backbone may be found in the molecules of several macrolide antibiotics

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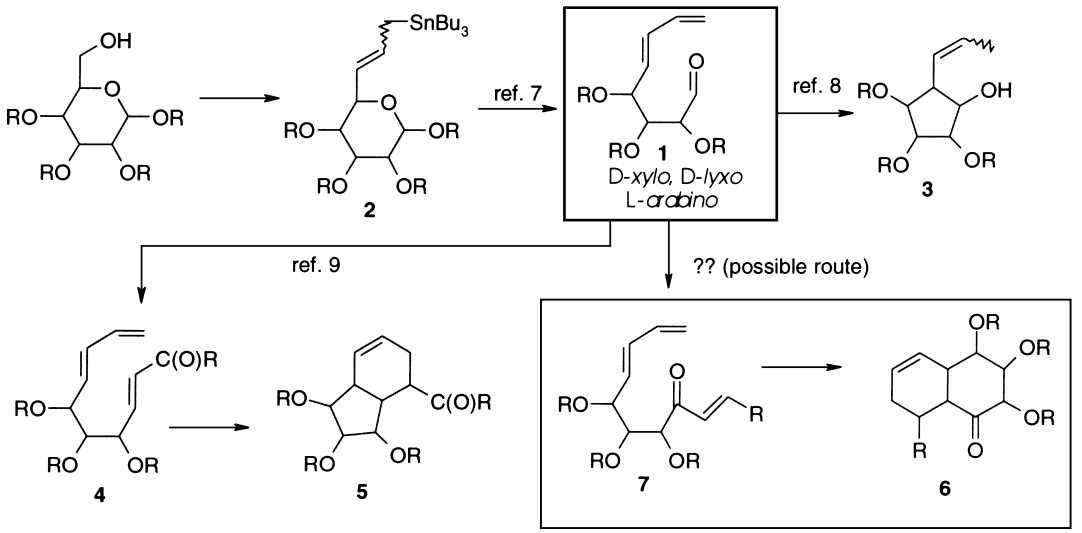
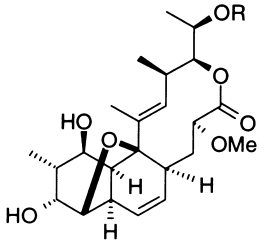


Figure 1. Preparation of enantiomerically pure carbocyclic derivatives from sugar allyltins

such as nodusmicin (R = H; isolated from *Saccharopolyspora hirsuta*[10]) or structurally related nargenicins (R = 2-pyrrolyl-CO-)[11] which are active against Gram-positive and drug resistant bacteria. The elegant and efficient synthesis of nargenicin A_1 via intramolecular Diels–Alder methodology has been recently accomplished by Roush.[6a]



nodusmicin
nargenicin

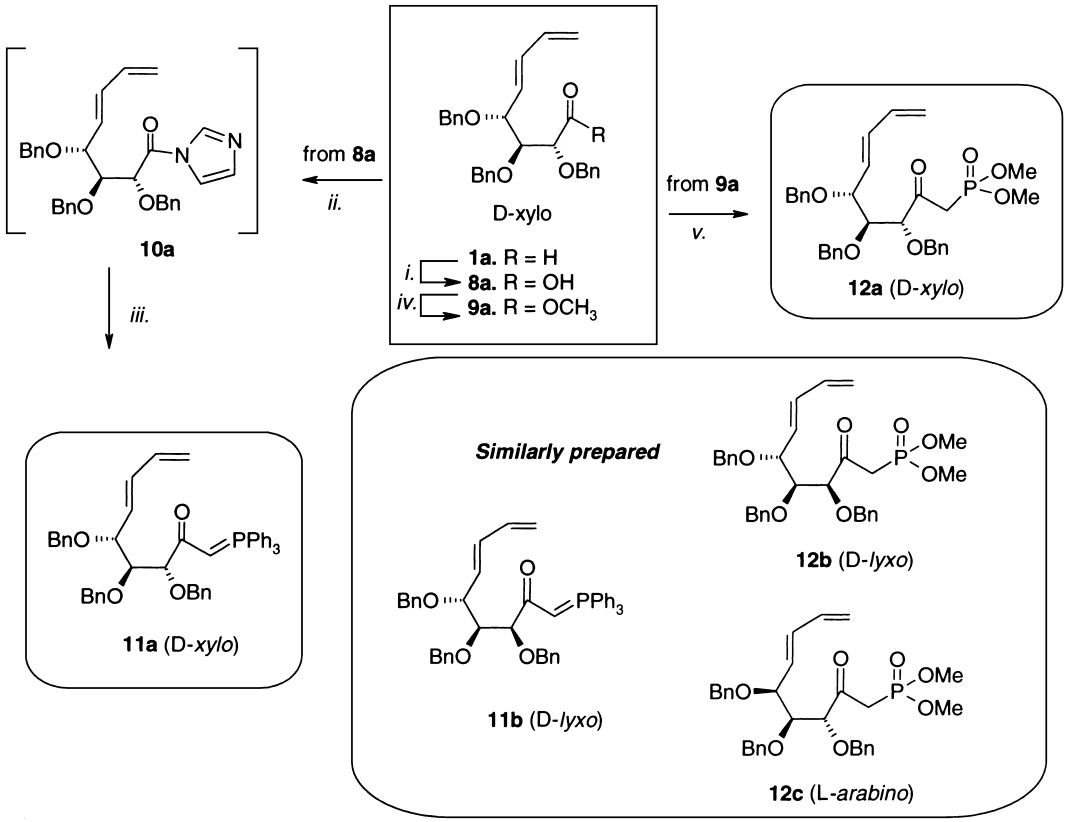
Application of dienoaldehyde **1** for the preparation of enantiomerically pure, highly oxygenated decalin system **6** requires a conversion of **1** into **7** (isomeric to **4**) followed by an intramolecular [4+2] cyclization of the latter. In this paper the model study on the stereoselective preparation of the bicyclo[4.4.0]decane system is presented.

2. Results and discussion

In order to convert the dienoaldehydes **1** into trienes **7** the hydrogen atom of the carbonyl group should be replaced with the olefinic moiety (–CH=CHR grouping). The Wittig-type methodology (i.e. conversion of simple monosaccharides into sugar phoshoranes[12] or phosphonates[13] and further reaction of such intermediates with sugar aldehydes) applied by us for the preparation of higher carbon sugars (having up to 21 carbon atoms in the chain[14]) opens a convenient route for such a transformation.

2.1. Preparation of Wittig-type reagents

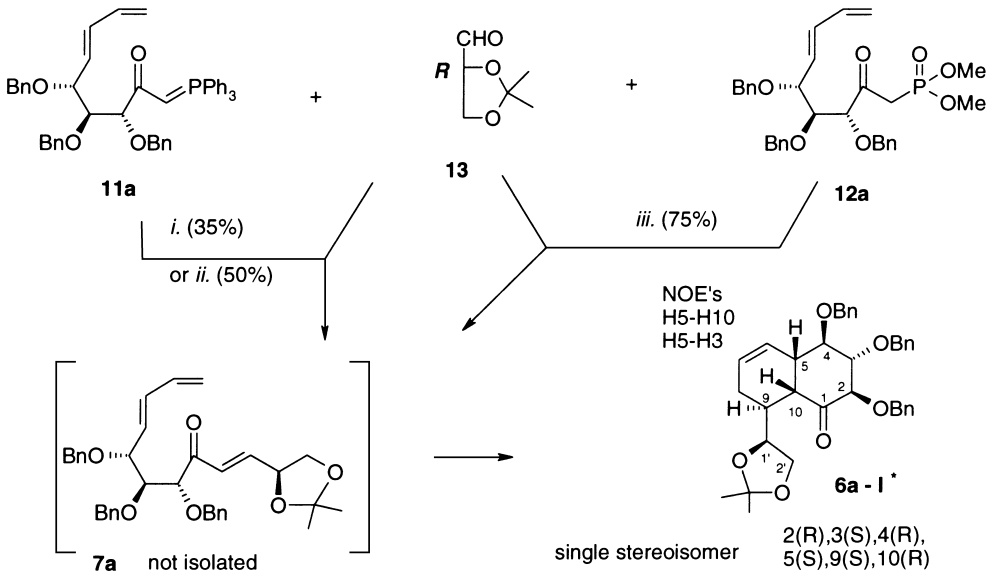
The synthesis of unsaturated sugar-derived phosphoranes and phosphonates is outlined in Scheme 1 (exemplified by conversion of aldehyde **1a** with the D-*xylo*-configuration at the three secondary carbinol centers into **11a** and **12a**).



Scheme 1. (i) Jones oxidation; (ii) *N*,*N*-carbonyl diimidazole, benzene, rt, 15 min; (iii) $Ph_3P{=}CH_2$ (3 equiv.), benzene, rt, 2 h, 55% from **8a**; (iv) CH_2N_2; (v) $MeP(O)(OMe)_2$, BuLi, THF, 15 min, 86%

Preparation of the D-*xylo*-phosphorane **11a** (a precursor of olefin **7**, cf. Fig. 1) essentially followed our method which works satisfactorily in higher sugar chemistry.[12] Thus, aldehyde **1a** was oxidized to acid **8a** with the Jones reagent and further treated with *N*,*N*-carbonyl diimidazole to afford reactive (and unstable) imidazolide **10a**. This compound was reacted with an excess of methylenetriphenylphosphorane ($Ph_3P{=}CH_2$) yielding the corresponding ylide **11a** with the D-*xylo*-configuration. Similarly, ylide **11b** (D-*lyxo*) was prepared from the appropriate aldehyde **1b**. Both ylides **11a** and **11b** were obtained in ca. 50%; all attempts to optimize the reaction conditions and to improve the yield of phosphoranes failed.

Sugar phosphonates represent an alternative to the ylides; we have observed, that they are usually more reactive towards sugar aldehydes and can be prepared in much higher yields than the corresponding phosphoranes.[14] The standard methodology[14] was applied for the preparation of phosphonates **12a**–**c**. Thus, aldonic acids **8a**–**c** were converted into methyl esters **9a**–**c** and



Scheme 2. (i) Xylene, reflux; (ii) toluene, 10 kbar; (iii) K_2CO_3, 18-crown-6, toluene, rt

treated with dimethyl methylphoshonate anion to afford phosphonates **12a–c** in ca. 80–85% yield (Scheme 1).

2.2. *Reaction of unsaturated Wittig-type intermediates with sugar aldehydes*

Efficient synthesis of a decalin system from carbohydrates requires the solution of at least two problems. The first one is the elaboration of an efficient method for the preparation of intermediate trienes, and the second one is concerned with the stereoselective cyclization of these reactive intermediates. For optimization of the conditions of the process, the reaction of phosphorane **11a** and phosphonate **12a** (with the D-*xylo*-configuration at the three consecutive stereogenic centers) with the simplest sugar aldehyde, *O*-isopropylidene-D-glyceraldehyde **13**, was studied (Scheme 2).

We observed, that phosphonate **11a** (which can be prepared in only 55% yield) did not react with aldehyde **13** under the standard conditions[12] applied in the preparation of higher carbon sugars, i.e. at room or slightly elevated temperature. The Wittig reaction took place at a much higher temperature (boiling xylene, ca. 140°C) and — under these conditions — the intermediate triene **7a** underwent spontaneous cyclization affording decalin **6a-I** as a single stereoisomer in 35% isolated yield; this was the only cyclic product formed.† We observed also significant decomposition of both substrates at this temperature.

Reaction of **11a** with **13** under high pressure (10 kbar) was more efficient and provided the same stereoisomer in 55% yield, again as the only cyclic product. Much better results were obtained by using the corresponding phosphonate **12a**; reaction of this material with **13** under

† Numbering of decalins **6**: letters **a**, **b**, and **c** refer to the configuration of the starting phosphonate (D-*xylo*-, D-*lyxo*- and L-*arabino*-, respectively); numbers: **I**, **II**, **III** refer to the aldehyde partner (**13**, **14**, and **15**; see also Scheme 2). The configurations of all decalins **6** were determined by NMR spectroscopy: COSY, HETCOR, NOE and/or NOESY. For details see Experimental and Schemes 3–5.

very mild phase transfer conditions (anhydrous toluene, 18-crown-6 at room temperature for 5 h) afforded the same cyclic product **6a-I** in 75% yield. It must be noted that even under these mild conditions (rt) cyclization of the intermediate triene occurred spontaneously. This was rather unexpected, since similar trienes **7′** are reported to be stable at room temperature and their cyclization to a decalin system is induced by high temperature or high pressure or a Lewis acid catalyst[15] (Fig. 2).

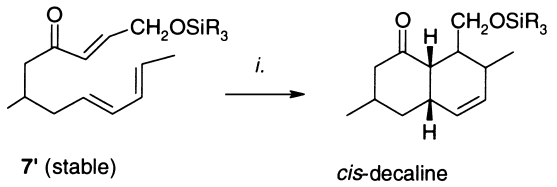
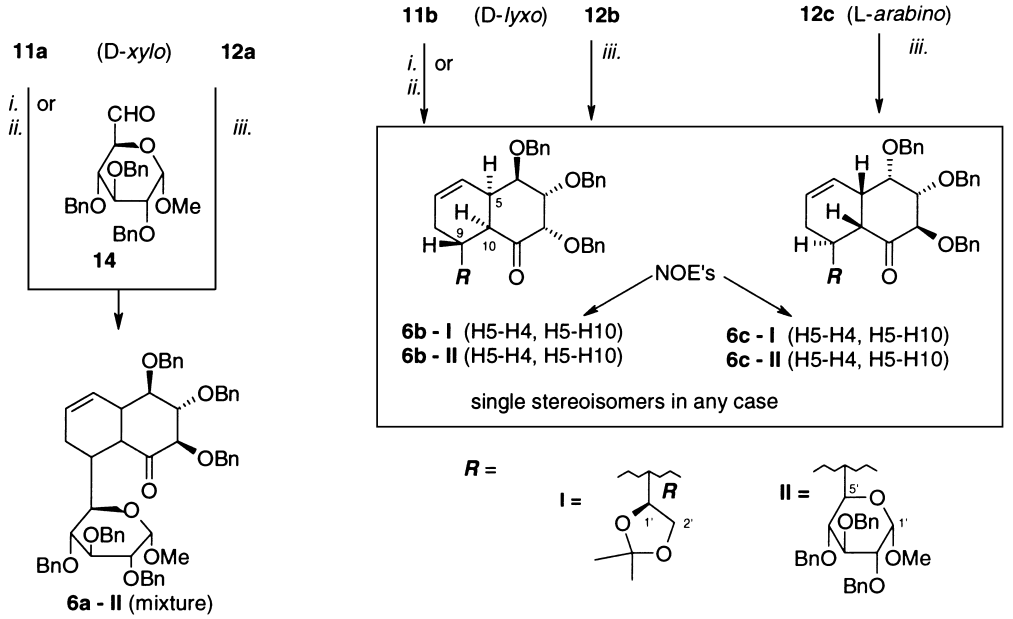


Figure 2. (i) 10 kbar, or PhCl reflux, or Et_2AlCl, 0°C

Only one stereosiomeric decalin was formed in all these reactions; the other important information from this model study is that the synthesis of chiral, highly oxygenated decalins can be performed much more conveniently using unsaturated phosphonates **12** instead of phosphoranes **11**. The yields are much higher in the case of **12** (preparation of **12** — 80%, reaction with aldehyde — 75% = 60% overall) than for **11** [preparation of **11** — 50%, reaction with aldehyde — 35% (thermal process) or 50% (high pressure) = 18% or 25% overall].

The stereochemical outcome of the reaction of **11a** or **12a** with the aldehyde having the opposite configuration at the C-α to the carbonyl group [methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-ulose **14**] significantly differed from that described above (with **13**). The reaction was not selective and a mixture of isomeric decalins **6a-II** was formed in this process (Scheme 3).



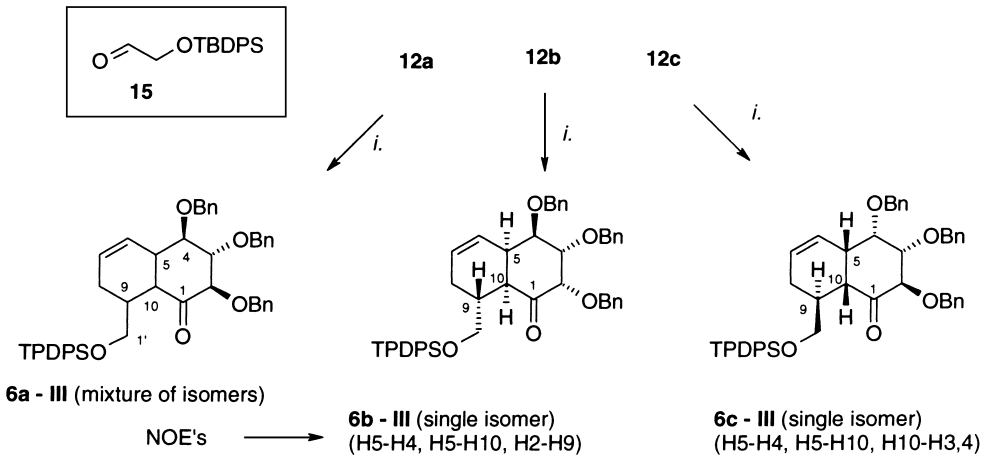
Scheme 3. (i) Xylene, reflux; (ii) toluene, 10 kbar; (iii) K_2CO_3, 18-crown-6, toluene, rt

On the basis of these results it might be postulated that the phosphonate **12a** or phosphorane **11a** having the D-*xylo*-configuration form the 'matched pair' with the *R* aldehyde (**13**) and the 'mismatched pair' with the *S* aldehyde **14**. The results obtained in the reactions of the Wittig-type reagents having the different configurations (D-*lyxo*-**11b** and **12b**, and L-*arabino*-**12c**) raised, however, the question if this simple statement ('matched mismatched pairs') is correct. The stereochemical outcome of the condensation of the D-*lyxo*-phosphorane **11b** or phosphonate **12b** with **13** and **14** was the same. Decalins **6b-I** and **6b-II** formed in this reaction had the same configuration at the three newly created stereogenic centers (at C5, C9 and C10) in both cases regardless of the configuration of the aldehyde used (*R*-**13** and *S*-**14**). The same trend was observed in reaction of phosphonate **12c** with both **13** and **14**. Again, the products: decalins **6c-I** and **6c-II** had the same configurations at C5,9,10 regardless of the configuration of the aldehyde used (Scheme 3).

The configurations at the newly created stereogenic centers in the latter products (**6c-I** and **6c-II**) were opposite to those formed in the reaction of the D-*lyxo*-ylides with aldehydes, namely decalins **6b-I** and **6b-II**. It is clear, therefore, that the configuration of the phosphorane or phosphonate itself is responsible for the stereochemical outcome of the formation of decalins **6**. To prove this hypothesis reaction of phosphonates **12a–c** with achiral aldehyde was studied.

2.3. Stereochemistry of the reaction of unsaturated phosphonates with achiral aldehyde

The simplest non-chiral sugar-like aldehyde, *O*-^{t}butyldiphenylsilyl glycoladehyde[16] (**15**) was chosen as the carbonyl substrate in the study of this asymmetric tandem Wittig-type Diels–Alder reaction leading to the [4.4.0]bicyclic system. Aldehyde **15** reacted readily with phosphonates **12** under very mild phase transfer conditions to afford the corresponding trienes (cf. Scheme 2) which underwent spontaneous cyclization under the reaction conditions yielding decalins **6-III**. The results are presented in Scheme 4.



Scheme 4. (i) K_2CO_3, 18-crown-6, toluene, rt

Reaction of **12a** (D-*xylo*-configuration) with **15** afforded decalin **6a-III** as a mixture of stereoisomers, while the condensation of the two other remaining phosphonates was highly stereoselective and led to decalins **6b-III** (from **12b**) and **6c-III** (from **12c**) with the same configuration at the newly created stereogenic centers as the corresponding products obtained in reactions of

12b and **12c** with chiral aldehydes. It is, therefore, clear that the stereochemistry of the cyclization process is governed by the configuration of the pre-existing stereogenic centers in the Wittig-type reagents and not those in the aldehyde partner.

2.4. Stereochemical aspects of the formation of decalins **6**

In all reactions studied in this paper only the *cis*-decalin system was formed. This is consistent with the literature data on the excellent *cis* selectivity in the intramolecular [4+2] cyclization of 1,7,9-decatrien-3-ones.[6,17] The transition state shown in Fig. 3 may explain this *cis* selectivity. Such arrangement of the reacting parts of the molecule (with the carbonyl group directed inside the diene system) allows for better overlapping of orbitals and, therefore, should lower the energy of the transition state of the intramolecular cyclization. Although the intermediate trienes **7** were not isolated (they underwent spontaneous cyclization under the reaction conditions) the *trans* geometry of the conjugated double bond could be expected on the basis of previous results.[18] Indeed, the *trans* relation between H<1> and H<2> protons in the final product **6** proved this assumption.

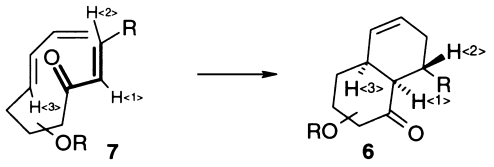


Figure 3. The model of the cyclization of decatrienes with the 'internal' activation of dienophile

The absolute stereochemistry of the tandem Wittig-type Diels–Alder reaction between unsaturated phosphonates and aldehydes is explained in Fig. 4. Triene **7a** (**I** or **II** or **III**) is formed in the condensation of the D-*xylo*-phosphonate **12a** with aldehydes **13**, **14** (both chiral, but having the opposite configuration at the C-α to the carbonyl group) or **15** (achiral), respectively. Similarly, trienes **7b** (**I**, **II**, **III**) and **7c** (**I**, **II**, **III**) were formed from phosphonates **12b** (D-*lyxo*) and **12c** (L-*arabino*). The transition states **A** and **A′** leading to the *cis*-decalin system are presented in Fig. 4.

Neither transition state in cyclization of **7a** is preferred; there are severe steric as well as Coulombic interactions in both **A** and **A′**. So, we should not expect the good selectivity unless the differentiation between both transition states would be possible by a (quite distant) chiral substituent at the dienophile part. Indeed, no, selectivity was observed in the reaction of **12a** with the achiral reagent ($R{=}CH_2OSiR_3$), but very high selectivity in the reaction with chiral aldehyde having the *R*-configuration at Cα (**13**; the opposite aldehyde *S*-**14**, however, also did not differentiate between **A** and **A′**).

The cyclization process of trienes **7b** (D-*lyxo*) and **7c** (L-*arabino*) is independent of the configuration of the substituent at the dienophile moiety (which is quite distant). The transition state **A′** is preferred over **A** in the cyclization of **7b** and **A** over **A′** in the cyclization of **7c** (see Fig. 2).

2.5. Model reaction of unsaturated phosphorus compounds with α-hydroxyaldehyde

Reaction of phosphorane **11a** with 3,4:5,6-di-*O*-isopropylidene-D-glucose (**16**, conveniently prepared from D-gluconolactone in three simple steps[19]) was studied. The phosphorane reacted more easily with such α-hydroxyaldehydes than with aldehydes without a free hydroxy group in the

molecule; at 80°C (boiling benzene) 53% of the cyclic product **6a-V′** was isolated after 20 h (140°C was required for reaction of **11a** with **13**, **14**, and **15**). Moreover, the yield of **6a-V′** was higher than **6a-I** (53% versus 35%). This is connected probably with the subsequent formation of the additional five-membered ring, i.e. cyclization of the ketoalcohol **6a-IV** to lactol **6a-V′** (Scheme 5).

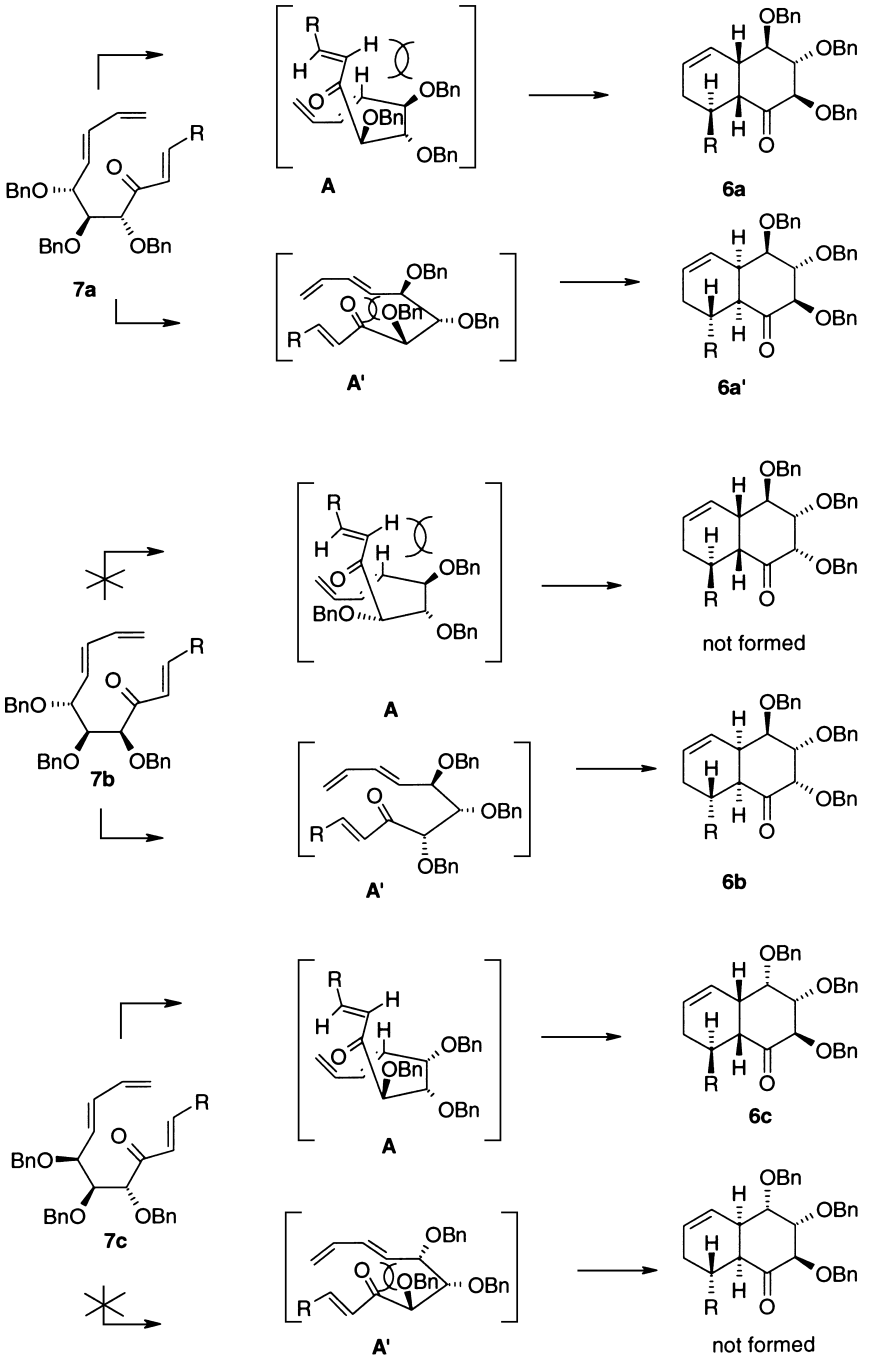
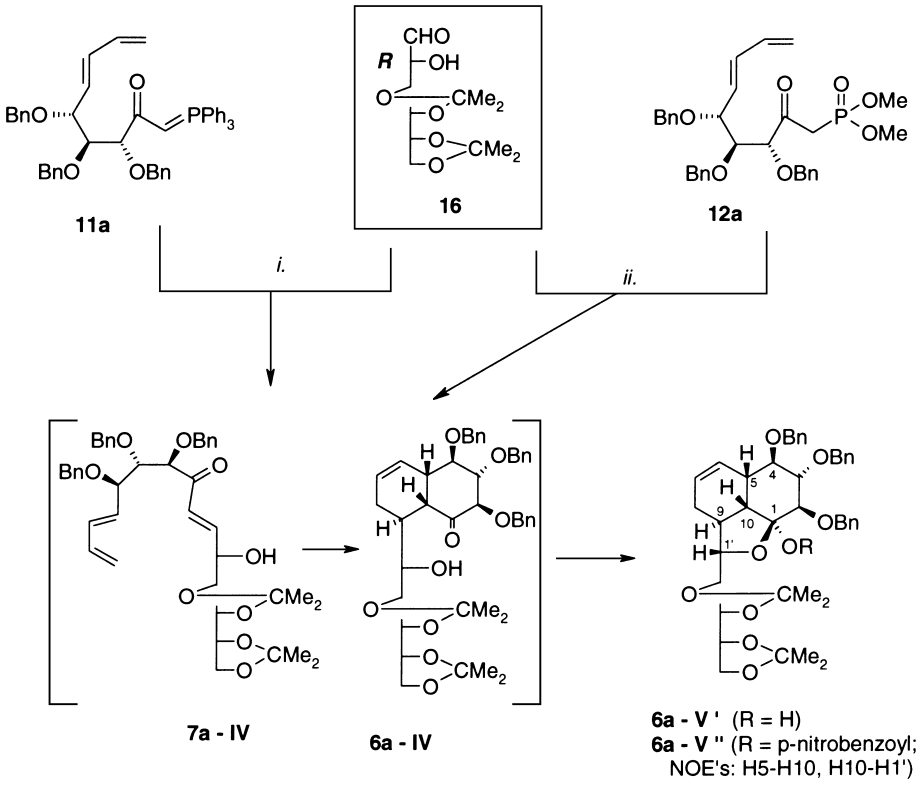


Figure 4. Transition states for cyclization of intermediate trienes **7**



Scheme 5. (i) **16**, benzene, reflux, 20 h; (ii) **16**, K_2CO_3, 18-crown-6, toluene, rt

Although the hydroxyaldehyde **16** is very unstable even under mild basic conditions,[19] it survived the phase transfer conditions used in the preparation of chiral decalins. Its toluene solution reacted with phosphonate **12a** in the presence of potassium carbonate and 18-crown-6 to afford product **6a-V′** in 75% yield, much better than in the reaction of **16** with phosphorane **11a**. Since in reactions of the D-*xylo*-phosphorus intermediates with the *R*-aldehyde only one isomer is formed (cf. **11a** or **12a+13→6a-I**), we expected the same selectivity in this reaction. Indeed, compound **6a-V′** was isolated as the only isomer from the reaction mixture and its configuration at the C5, C9 and C10 centers was the same as in **6a-I**.

The configuration of decalin **6a-V′** was also assigned from the high-resolution NMR spectra. Since the appropriate diagnostic signals overlapped in **6a-V′**, the compound was converted into *p*-nitrobenzoyl ester **6a-V″** in the spectrum of which the corresponding NOEs between H5–H10 (6%) and H10–H1′ (4.5%) were seen. The resonance of the C1 atom was also observed at $\delta = 109.0$, which indicated the presence of the five-membered heterocyclic ring in the molecule.

3. Conclusion

The highly oxygenated decalin derivatives **6** could be obtained by reaction of sugar-derived unsaturated phosphoranes **11a**,**b** or phosphonates **12a**–**c** with aldehydes. The latter process is more convenient and allows preparing the carbobicyclic products **6** in much higher yields and under milder conditions. There is no difference in the stereochemical outcome of the process

conducted with either phosphorane or phosphonate (with the same configuration at the three carbinol centers). Preparation of decalins **6** from phosphonates or phosphoranes and aldehydes consists of two steps: (i) formation of a triene intermediate in the Wittig-type reaction and (ii) cyclization of the latter. The second step (cyclization) occurs spontaneously under the conditions of the Wittig-type reaction and the intermediate triene cannot be isolated.

The stereochemistry of this tandem Wittig-type Diels–Alder reaction depends solely on the geometry of the starting phosphoranes or phosphonates having the D-*lyxo*- and L-*arabino*-configurations **11b**, **12b**, and **12c** and does not depend on the configuration of the aldehyde used, *R*-**13**, *S*-**14** or achiral **15**. However, for the D-*xylo*-phosphorus substrates **11a** and **12a** the situation is different; the configuration of the product depends on the configuration of the aldehyde used **13** and does not depend on the chirality of the phosphorus substrates.

4. Experimental

4.1. General

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) and DEPT correlations. The relative configurations of the protons were determined by NOE or NOESY experiments. Mass spectra [LSIMS (*m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added) or EI] were recorded with an AMD-604 (AMD Intectra GmbH, Germany) mass spectrometer. Specific rotations were measured with a JASCO DIP Digital Polarimeter for chloroform solution (c~1.5) at room temperature. Column chromatography was performed on silica gel (Merck, 70–230 and 230–400 mesh). Organic solutions were dried over anhydrous magnesium sulfate. All reactions with BuLi were performed under an argon atmosphere. 2,3,4-Tri-*O*-benzyl-oct-5(*E*),7-dieno-D-xylose **1a**, 2,3,4-tri-*O*-benzyl-oct-5(*E*),7-dieno-D-lyxose **1b**, and 2,3,4-tri-*O*-benzyl-oct-5(*E*),7-dieno-L-arabinose **1c** were prepared according to Ref. 7. Aldehydes **13**, **14**, **15**, and **16** were prepared directly before use; 2,3-*O*-isopropylidene-D-glyceraldehyde **13** by a cleavage of diacetono-mannitol with $NaIO_4$,[20] methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-ulose **14** by a Swern oxidation[21] of the parent alcohol, *O*-*t*butyldiphenylsilyl glycoladehyde[16,22] **15** from the protected allyl alcohol by a cleavage of the double bond with ozone followed by reduction with Me_2S, and 3,4:5,6-di-*O*-isopropylidene-D-glucose **16** from D-gluconolactone according to Ref. 19.

4.2. Preparation of unsaturated aldonic acids

To a solution of appropriate dienoaldehyde[7] **1a**, **1b**, or **1c** (1 mmol) in acetone (10 mL) a solution of Jones reagent[23] in water was added until TLC (hexane:ethyl acetate, 3:1) indicated the disappearance of a starting material and formation of a new very polar product, acid **8a**–**c**. The mixture was partitioned between ethyl acetate and brine, the organic layer was separated, washed with water, dried and the crude acid (obtained in ca. 90% yield) was characterized as methyl ester **9a**–**c** (obtained by reaction of the crude product with diazomethane).

4.2.1. Methyl 2,3,4-tri-O-benzyl-oct-5(E),7-dieno-D-xylonate **9a**

85%; $[\alpha]_D$ +50. ^1H NMR (200 MHz) δ 6.22 (m, H-6,7), 5.49 (dd, $J_{4,5}$ 7.7, $J_{5,6}$ 14.5, H-5), 5.13 (m, both H-8), 4.22 (dd, $J_{3,4}$ 7.5, H-4), 4.08 (d, $J_{2,3}$ 3.3, H-2), 3.91 (dd, H-3), 3.55 (OMe). ^{13}C

NMR δ 171.0 (C-1), 136.0, 134.9, 129.9 (C-5,6,7), 118.2 (C-8), 82.0, 80.8, 78.6 (C-2,3,4), 74.9, 73.1, 71.0 (3×*C*H_2Ph), 51.7 (O*Me*). HRMS *m*/*z*: 495.2153 [$C_{30}H_{32}O_5Na$ (M+Na^+) requires 495.2147].

*4.2.2. Methyl 2,3,4-tri-*O*-benzyl-oct-5(*E*),7-dieno-D-lyxonate* ***9b***

79%; $[\alpha]_D$ –51.9. ^{1}H NMR (200 MHz) inter alia δ 6.30 (m, H-6,7), 5.67 (dd, $J_{4,5}$ 7.8, $J_{5,6}$ 14.7, H-5), 5.19 (m, both H-8), 3.62 (OMe). ^{13}C NMR δ 171.5 (C-1), 136.1, 134.6, 130.6 (C-5,6,7), 118.0 (C-8), 82.8, 79.3, 78.4 (C-2,3,4), 74.8, 72.6, 70.6 (3×*C*H_2Ph), 51.8 (O*Me*). HRMS *m*/*z*: 495.2124 [$C_{30}H_{32}O_5Na$ (M+Na^+) requires 495.2147].

*4.2.3. Methyl 2,3,4-tri-*O*-benzyl-oct-5(*E*),7-dieno-L-arabinate* ***9c***

81%; $[\alpha]_D$ +16.9. ^{1}H NMR (200 MHz) inter alia δ 6.39 (m, H-6,7), 5.68 (dd, $J_{4,5}$ 7.9, $J_{5,6}$ 14.7, H-5), 5.13 (m, both H-8), 3.9 (dd, $J_{3,4}$ 3.3, H-4), 3.59 (OMe). ^{13}C NMR δ 171.7 (C-1), 136.1, 135.6, 131.3 (C-5,6,7), 118.1 (C-8), 81.7, 78.5, 78.3 (C-2,3,4), 74.3, 73.2, 70.2 (3×*C*H_2Ph), 51.7 (O*Me*). HRMS *m*/*z*: 495.2140 [$C_{30}H_{32}O_5Na$ (M+Na^+) requires 495.2147].

4.3. Preparation of unsaturated phosphoranes

To a solution of the aldonic acid **8a** or **8b** (1 mmol) in benzene (10 mL) under an argon atmosphere, *N*,*N*′-carbonyldiimidazole (195 mg, 1.2 equiv.) was added in one portion and the mixture was stirred at room temperature until evolution of the gaseous products ceased (ca. 15 min). This solution of crude imidazolide **10a** or **10b** was then added to a solution of $Ph_3P{=}CH_2$ (3 equiv., generated from 1.22 g of Ph_3PCH_3I and 1.2 mL of 2.5 M BuLi in benzene at rt for 2 h), the mixture was stirred for 2 h at rt, partitioned between ethyl acetate and brine, the organic layer was separated, washed with water, dried and concentrated and the product was purified by column chromatography (hexane:ethyl acetate, 2:1→1:4) to afford ylides **11a** (55%) or **11b** (50%), respectively. These compounds were characterized only by HRMS: **11a** *m*/*z*: 717.3131; **11b** *m*/*z*: 717.3130 [$C_{48}H_{46}O_4P$ (M+H^+) requires 717.3134].

All attempts to optimize the yield (changing the solvent for THF, lowering the temperature etc.) failed.

4.4. Preparation of unsaturated phosphonates

To a cooled –78°C solution of dimethyl methylphosphonate (0.313 mL, 2.93 mmol) in dry THF (20 mL), a 2.5 M solution of butyllithium in hexane (1.14 mL, 2.85 mmol) was added and the mixture was stirred at –78°C for 30 min. Appropriate methyl ester **9a**–**c** (0.6 mmol) was added in ca. 5 min by a syringe, the mixture was stirred at –78°C for 30 min, partitioned between ethyl acetate and brine, the organic layer was separated, washed with water, dried, and concentrated and the crude phosphonate was isolated by column chromatography (hexane:ethyl acetate, 4:1→1:2).

*4.4.1. Dimethyl [2-keto-(3*R*,4*S*,5*R*)-tri-*O*-benzyl-6(*E*),8-dienonon-1-yl]phosphonate* ***12a***

86%; ^{1}H NMR (200 MHz) δ 6.24 (m, H-6,7), 5.59 (dd, $J_{4,5}$ 7.8, $J_{5,6}$ 14.5, H-5), 5.15 (m, both H-8), 4.03 (dd, $J_{3,4}$ 4.4, H-4), 3.70 and 3.64 (2d, $J_{P,H}$ 4.2 and 4.6, 2×OMe), 3.36 and 2.91 [both CH_2P(O)(OMe)$_2$ (dd, $J_{H,H}$ 14.5, $J_{H,P}$ 22.0) and (dd, $J_{H,P}$ 20.9)]. ^{13}C NMR δ 200.8 (d, $J_{C,P}$ 6.2, C-1), 135.9, 134.6, 130.0 (C-5,6,7), 118.2 (C-8), 82.5, 82.1, 79.0 (C-2,3,4), 73.8, 72.8, 71.0 (3×*C*H_2Ph), 52.7 and 51.9 (2d, both $J_{C,P}$ 6.3, 2×O*Me*), 38.4 [d, $J_{C,P}$ 128, *C*H_2P(O)(OMe)$_2$]. HRMS *m*/*z*: 587.2162 [$C_{32}H_{37}O_7PNa$ (M+Na^+) requires 587.2175].

*4.4.2. Dimethyl [2-keto-(3*S*,4*S*,5*R*)-tri-*O*-benzyl-6(*E*),8-dienonon-1-yl]phosphonate* ***12b***

81%; ^{1}H NMR (200 MHz) δ 6.24 (m, H-6,7), 5.59 (dd, $J_{4,5}$ 8.0, $J_{5,6}$ 14.3, H-5), 5.15 (m, both H-8), 4.11 (dd, $J_{3,4}$ 6.0, H-4), 3.89 (dd, $J_{2,3}$ 4.0, H-3), 3.71 and 3.69 (2d, $J_{P,H}$ 4.0 and 4.8, 2×OMe), 3.46 and 3.02 [both CH_2P(O)(OMe)$_2$ (dd, $J_{H,H}$ 14.6, $J_{H,P}$ 20.7) and (dd, $J_{H,P}$ 22.2)]. ^{13}C NMR δ 202.8 (d, $J_{C,P}$ 7.0, C-1), 135.8, 135.1, 130.3 (C-5,6,7), 118.3 (C8), 83.7, 83.5, 80.0 (C-2,3,4), 74.5, 72.8, 70.6 (3×*C*H$_2$Ph), 52.7 and 52.6 (2d, both $J_{C,P}$ 6.3, 2×O*Me*), 37.9 [d, $J_{C,P}$ 130, *C*H$_2$P(O)(OMe)$_2$]. HRMS *m*/*z*: 587.21801 [$C_{32}H_{37}O_7PNa$ (M+Na$^+$) requires 587.2175].

*4.4.3. Dimethyl [2-keto-(3*R*,4*S*,5*S*)-tri-*O*-benzyl-6(*E*),8-dienonon-1-yl]phosphonate* ***12c***

82%; ^{1}H NMR (200 MHz) δ 6.37 (m, H-6,7), 5.69 (dd, $J_{4,5}$ 8.1, $J_{5,6}$ 14.1, H-5), 5.20 (m, both H-8), 4.10 (dd, $J_{3,4}$ 7.1, H-4), 3.85 (dd, $J_{2,3}$ 3.5, H-3), 3.71 and 3.65 (2d, $J_{P,H}$ 7.7 and 7.6, 2×OMe), 3.15 [center of multiplet of both CH_2P(O)(OMe)$_2$]. ^{13}C NMR δ 203.3 (d, $J_{C,P}$ 6.1, C1), 136.1, 135.9, 130.6 (C-5,6,7), 118.5 (C-8), 84.6, 81.9, 78.9 (C-2,3,4), 74.3, 73.5, 70.1 (3×*C*H$_2$Ph), 52.7 and 52.6 (2d, $J_{C,P}$ 5.8 and 5.9, 2×O*Me*) [d, $J_{C,P}$ 132, *C*H$_2$P(O)(OMe)$_2$]. HRMS *m*/*z*: 587.2207 [$C_{32}H_{37}O_7PNa$ (M+Na$^+$) requires 587.2175].

4.5. Reaction of unsaturated phosphoranes with aldehydes

4.5.1. Under atmospheric pressure

To a solution of phosphorane **11a** or **11b** (0.5 mmol) in xylene (15 mL), appropriate aldehyde **13** or **14** was added (0.5 mmol) and the reaction mixture was boiled under reflux for 30 h. After that time TLC (hexane:ethyl acetate, 1:1) indicated disappearance of the very polar ylide and formation of a less polar product (under these harsh conditions both, the aldehyde and dienophosphorane underwent considerable decomposition). The solvent was evaporated and the residue was purified by column chromatography (hexane:ethyl acetate, 5:1→3:1) to afford:

- **6a-I** (from **11a** and **13**) in 35% yield as the only cyclic product (for characterization of all pure isomers see Section 4.7).
- **6a-II** (from **11a** and **14**) in 40% yield as an inseparable mixture of decalins; MS *m*/*z*: 923.4149 [$C_{58}H_{60}O_9Na$ (M+Na$^+$) requires 923.4135]. Two major products were seen (ratio ca. 1:1) in the NMR spectra [^{1}H- 3.49, 3.34 (OMe) and ^{13}C- 98.2, 97.7 ppm (C1 of glucose moiety)]. Signals at 3.10, 2.89 (H5 of both isomers), 34.4, 31.2 ppm (C5), 2.64, 2.46 (H10), 49.9, 43.6 (C10), and 5.85–5.6 (H6,7), 129.8, 127.4, 126.2, 123.0 (C7,8) proved the decalin structure of both isomers **6a-II**.
- **6b-II** (from **11b** and **14**) in 45% yield as the only cyclic product.

4.5.2. Under high pressure

A solution of **11a** or **11b** (ca. 0.5 mmol) and aldehyde **13** or **14** in a toluene:benzene mixture (4:1 v/v, 11 mL) was placed in a piston-cylinder type apparatus[24] under 10 kbar for 2 days at room temperature. Products were isolated by column chromatography as described above to afford:

- **6a-I** (from **11a** and **13**) in 55% yield as the only cyclic product.
- **6a-II** (from **11a** and **14**) in 50% yield (ca. 1:1 mixture of isomers, the same as in thermal reaction).
- **6b-II** (from **11b** and **14**) in 60% yield as the only cyclic product.

4.6. Reaction of unsaturated phosphonates with aldehydes

To a solution of phosphonate **12a**, or **12b**, or **12c** (1 mmol) and aldehyde **13**, or **14**, or **15** in anhydrous toluene (20 mL) anhydrous potassium carbonate (ca. 0.5 g) was added followed by a catalytic amount (ca. 30 mg) of 18-crown-6. The mixture was stirred at room temperature until TLC (hexane:ethyl acetate, 3:1) indicated disappearance of both starting materials and formation of a new product (2–6 h). The mixture was diluted with ethyl acetate (30 mL), washed with water, dried and concentrated and the products were isolated by column chromatography (hexane:ethyl acetate, 6:1) to afford:

- **6a-I** (from **12a** and **13**); 75%.
- **6b-I** (from **12b** and **13**); 75%.
- **6c-I** (from **12c** and **13**); 72%.
- **6a-II** (from **12a** and **14**); 80%; ca. 1:1 mixture of (the same as in **11a+13**).
- **6b-II** (from **12b** and **14**); 72%.
- **6c-II** (from **12c** and **14**); 76%.
- 6a-**III** (from **12a** and **15**); 63% (inseparable mixture of at least three stereoisomers as detected by HPLC (hexane:ethyl acetate, 10:1); HRMS for the mixture *m*/*z*: 759.3512 [$C_{48}H_{52}O_5NaSi$ ($M+Na^+$) requires 759.3481].
- **6b-III** (from **12b** and **15**); 71%.
- **6c-III** (from **12c** and **15**); 60%.

4.7. Characterization of enantiomerically pure decalins **6**

4.7.1. (2R,3S,4R,5S,9S,10R)-{1-Keto-2,3,4-tri-O-benzyl-6,7-ene-9-[1′(R)-5,5-dimethyl-2,4-dioxolane-1′-yl]}decalin **6a-I**

$[\alpha]_D$ +123.1. ^{1}H NMR δ 6.01 (m, H-7), 5.75 (m, H-6), 4.65 (d, $J_{2,3}$ 10.2, H-2), 4.03 (dd, $J_{1',2'}$ 5.5, $J_{2',2'}$ 8.1, H-2′a), 3.90 (m, H-1′), 3.82 (dd, $J_{3,4}$ 9.1, $J_{4,5}$ 10.5, H-4), 3.68 (dd, H-3), 3.53 (dd, $J_{1',2'}$ 8.8, H-2′b), 2.56 (dd, $J_{9,10}$ 11.8, $J_{5,10}$ 5.6, H-10), 2.42 (m, H-5), 2.19 (m, H-9), 1.78 and 2.01 (2m, both H-8), 1.30 (6H, CMe_2). ^{13}C NMR δ 207.0 (C1), 127.8 and 126.0 (C6,7), 109.4 (CMe$_2$), 85.6 (C2), 85.5 (C3), 83.3 (C4), 78.7 (C1′), 76.0, 75.7 and 72.8 (3×OBn), 67.8 (C2′), 53.5 (C10), 38.6 (C5), 37.5 (C9), 27.2 (C8), 26.9 and 26.1 (CMe_2) ppm. NOEs: H5–H10 (7%), H5–H3 (4%), H4–H9 (7%), H2–H9 (7%). HRMS *m*/*z*: 591.2762 [$C_{36}H_{40}O_6Na$ ($M+Na^+$) requires 591.2723].

4.7.2. (2S,3S,4R,5R,9R,10S)-{1-Keto-2,3,4-tri-O-benzyl-6,7-ene-9-[1′(R)-5,5-dimethyl-2,4-dioxolane-1′-yl]}decalin **6b-I**

$[\alpha]_D$ –96.6. ^{1}H NMR δ 5.84 and 5.65 (2m, H-6,7), ~4.5 (H-2), 3.96 (dd, $J_{2,3}$ 2.8, $J_{3,4}$ 5.5, H-3), 3.91 (m, H-1′), 3.84 (m, H-2′a), 3.81 (dd, $J_{4,5}$ 4.2, H-4), 3.50 (m, H-2′b), 2.94 (m, H-5), 2.64 (m, H-10), 2.60 (m, H-9), 2.25 and 1.94 (2m, both H-8), 1.37 and 1.32 (CMe_2). ^{13}C NMR δ 208.1 (C-1), 128.0 and 124.9 (C-6,7), 108.7 (CMe$_2$), 80.6 (C-2), 79.9 (C-3), 78.1 (C-1′), 77.5 (C-4), 73.1, 73.0 and 72.3 (3×OBn), 66.6 (C-2′), 50.0 (C-10), 37.2 (C-5), 35.1 (C-9), 26.3 (C-8), 26.2 and 25.6 (CMe_2). NOESY: H5–H10, H5–H4, H9–H2. HRMS *m*/*z*: 591.2732 [$C_{36}H_{40}O_6Na$ ($M+Na^+$) requires 591.2723].

4.7.3. (2R,3S,4S,5S,9S,10R)-{1-Keto-2,3,4-tri-O-benzyl-6,7-ene-9-[1′(R)-5,5-dimethyl-2,4-dioxolane-2′-yl]}decalin **6c-I**

$[\alpha]_D$ +31.4. ^{1}H NMR δ 5.65 (m, H-7), 5.15 (dd, $J_{6,7}$ 10.1, $J_{5,6}$ 1.5, H-6), 4.54 (d, $J_{2,3}$ 10.4, H-2), 3.92 (m, H-1′,2′a), 3.87 (dd, $J_{3,4}$ 2.6, $J_{4,5}$ 3.0, H-4), 3.62 (dd, H-3), 3.50 (m, H-2b′), 2.82 (m, H-5),

2.59 (m, H-10), 2.48 (m, H-9), 2.35 and 2.17 (2m, both H-8), 1.37 and 1.33 (C*Me*$_2$). ^{13}C NMR δ 206.0 (C-1), 129.8 (C-7), 123.8 (C-6), 108.7 (*C*Me$_2$), 84.5 (C-2), 80.4 (C-3), 78.9 (C-2), 77.0 (C-1′), 74.2, 73.7 and 72.0 (3×OBn), 68.0 (C-2′), 43.9 (C-10), 35.2 (C-5), 33.8 (C-9), 26.7 and 25.8 (C*Me*$_2$), 23.5 (C8). NOESY: H5–H10, H5–H4, H9–H2. HRMS *m*/*z*: 591.2728 [$C_{36}H_{40}O_6Na$ (M+Na$^+$) requires 591.2723].

*4.7.4. (2*S*,3*S*,4*R*,5*R*,9*R*,10*S*)-[1-Keto-2,3,4-tri*-O-*benzyl-6,7-ene-9-(methyl 2,3,4-tri*-O-*benzyl-α-*D*-glucopyranosid-5-yl)]decalin* ***6b-II***

^{1}H NMR δ 5.75 (m, H-6,7), 4.52 (d, $J_{1',2'}$ 3.5, H-1′), 4.40 (d, $J_{2,3}$ 2.3, H-2), 4.00 (dd, $J_{2',3'}$ 9.3, $J_{3',4'}$ 9.0, H-3′), 3.94 (dd, $J_{3,4}$ 6.6, $J_{4,5}$ 4.3, H-4), 3.85 (dd, H-3), 3.62 (dd, $J_{4',5'}$ 9.6, $J_{5',9}$ 5.9, H-5′), 3.44 (dd, H-2′), 3.38 (OMe), 3.33 (dd, H-4′), 3.03 (m, H-5), 2.98 (dd, $J_{9,10}$ 7.0, $J_{5,10}$ 6.4, H-10), 2.91 (m, H-9), 2.39 and 2.06 (2m, both H8). ^{13}C NMR δ 128.9 and 124.5 (C-6,7), 97.6 (C-1′), 82.1 (C-3′), 81.4 (C-4′), 81.1 (C-2), 80.1 (C-2′), 79.9 (C-3), 78.1 (C-4), 72.6 (C-5′), 56.3 (OMe), 48.5 (C-10), 37.0 (C-5), 34.5 (C-9), 28.0 (C-8). NOEs: H4–H5 (6%), H4–H10 (3%); NOESY: H5–H10, H9–H2. HRMS *m*/*z*: 923.4146 [$C_{58}H_{60}O_9Na$ (M+Na$^+$) requires 923.4135].

*4.7.5. (2*R*,3*S*,4*S*,5*S*,9*S*,10*R*)-[1-Keto-2,3,4-tri*-O-*benzyl-6,7-ene-9-(methyl 2,3,4-tri*-O-*benzyl-α-*D*-glucopyranosid-5-yl)]decalin* ***6c-II***

$[\alpha]_D$ +40.8. ^{1}H NMR δ 5.56 and 5.08 (2m, H-6,7), 4.48 (d, $J_{1',2'}$ 3.5, H-1′), 4.42 (d, $J_{2,3}$ 10.4, H-2), 3.97 (dd, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.1, H-3′), 3.80 (dd, $J_{3,4}$ 2.4, $J_{4,5}$ 2.7, H-4), 3.68 (dd, $J_{4',5'}$ 9.6, $J_{5',9}$ 5.6, H-5′), 3.58 (dd, H-3), 3.43 (dd, H-2′), 3.35 (dd, H-4′), 3.31 (OMe), 3.08 (m, H-5), 2.92 (m, H-10), 2.89 (m, H-9), 2.49 and 2.05 (2m, both H-8). ^{13}C NMR δ 206.1 (C-1), 129.8 and 124.2 (C-6,7), 97.8 (C-1′), 84.7 (C-2), 82.5 (C-3′), 80.6 (C-3), 80.1 (C-2′), 80.0 (C-4′), 78.6 (C-4), 72.4 (C-5′), 55.6 (OMe), 42.2 (C-10), 35.7 (C-5), 30.5 (C-9), 26.0 (C-8). NOESY: H5–H4, H5–H10. Anal. calcd for $C_{58}H_{60}O_9$: C, 77.31; H, 6.71. Found: C, 77.20; H, 6.61.

*4.7.6. (2*S*,3*S*,4*R*,5*R*,9*R*,10*S*)-[1-Keto-2,3,4-tri*-O-*benzyl-6,7-ene-9-(*t*-butyldiphenyl sililoxymethyl-ene)]decalin* ***6b-III***

$[\alpha]_D$ –63.0. ^{1}H NMR δ 5.83 (m, H-7), 5.67 (m, H-6), 4.32 (d, $J_{2,3}$ 2.6, H-2), 3.96 (dd, $J_{3,4}$ 5.7, H-3), 3.89 (dd, $J_{4,5}$ 4.2, H-4), 3.49 (d, *J* 6.8, both H-1′), 2.96 (m, H-5), 2.82 (dd, $J_{9,10}$ 8.8, $J_{5.10}$ 6.2, H-10), 2.62 (m, H-9), 2.45 and 1.88 (both H-8). ^{13}C NMR δ 208.9 (C-1), 129.6 (C-7), 124.7 (C-6), 81.0 (C-2), 80.3 (C-3), 78.2 (C-4), 73.2, 73.0 and 72.1 (3×OBn), 65.8 (C-1′), 49.1 (C-10), 36.6 (C-5), 34.9 (C-9), 27.6 (C8) ppm. NOESY: H5–H10, H5–H4, H2–H9, H5–H1′, H10–H1′. HRMS *m*/*z*: 759.3508 [$C_{48}H_{52}O_5SiNa$ (M+Na$^+$) requires 759.3482].

*4.7.7. (2*R*,3*S*,4*S*,5*S*,9*S*,10*R*)-[1-Keto-2,3,4-tri*-O-*benzyl-6,7-ene-9-(*t*-butyldiphenyl sililoxymethyl-ene)]decalin* ***6c-III***

$[\alpha]_D$ +12.2. ^{1}H NMR δ 5.52 (m, H-7), 5.09 (dd, $J_{6,7}$ 10.1, $J_{5,6}$ ~1, H-6), 4.63 (d, $J_{2,3}$ 10.3, H-2), 3.91 (dd, $J_{3,4}$ 2.5, $J_{4,5}$ 3.0, H-4), 3.62 (dd, H-3), 3.54 (dd, $J_{1',1'}$ 10.0, $J_{1',9}$ 10.0, H-1′a), 3.46 (dd, $J_{1',9}$ 9.9, H-1′b), 3.19 (H-10), 2.92 (m, H-5), 2.71 (m, H-9), 2.36 and 1.61 (both H-8). ^{13}C NMR δ 207.8 (C-1), 129.2, (C-7), 124.2 (C-6), 84.9 (C-2), 80.7 (C-3), 78.5 (C-4), 74.3, 73.7 and 72.5 (3×OBn), 64.8 (C-1′), 42.5 (C-10), 34.0 (C-5), 32.49 (C-9), 24.0 (C-8) ppm. NOESY: H5–H10, H5–H4, H10–H1′a1′b; there is also the NOE between H9–H10, but although these protons are in the *trans* relation, they are close because of the preferred conformation of the bicyclic system (H9–H10 are gauche-arranged). HRMS *m*/*z*: 759.3546 [$C_{48}H_{52}O_5SiNa$ (M+Na$^+$) requires 759.3482]. Anal. calcd for $C_{48}H_{52}O_5Si{\cdot}1/2H_2O$: C, 77.28; H, 7.03. Found: C, 77.36; H, 6.88.

4.8. Preparation of decalin **6a-V′**

4.8.1. Reaction of α-hydroxyaldehyde **16** with phosphorane **11a**

Under atmospheric pressure: Phosphorane **11a** (0.35 g, 0.49 mmol) and aldehyde **16** (0.15 g, 0.58 mmol) in dry benzene (10 mL) were heated under reflux until TLC (hexane:ethyl acetate, 1:1) indicated disappearance of ylide **11a** (20 h). Solvent was evaporated under reduced pressure and the product was isolated by column chromatography (hexane:ethyl acetate, 6:1→3:1) to afford decalin **6-V′** as a single isomer (180 mg, 0.26 mmol, 53%); MS *m/z*: 721.3349 [$C_{42}H_{50}O_9Na$ ($M+Na^+$) requires 721.3352]. No carbonyl absorption in the IR spectrum of **6a-V′** was observed. In the 500 MHz ^1H NMR spectrum most of the diagnostic signals overlapped, however the ^{13}C NMR data proved the bicyclic structure: ^{13}C NMR inter alia δ 109.8 and 109.0 (2×*C*Me$_2$), 104.2 (C-1), 47.8 (C-10), 37.8 and 37.2 (C-5,9), 27.9 (C-8). For better characterization this compound was converted into the *p*-nitrobenzoyl derivative **6-V″** by action of *p*-nitrobenzoyl chloride on a solution of **6-V′** in CH_2Cl_2 in the presence of triethylamine and DMAP.

*4.8.1.1. (1*R*,2*R*,3*S*,4*R*,5*S*,9*S*,10*R*)-{1*-O-p-*Methoxybenzoyl-2,3,4-tri*-O-*benzyl-6,7-ene-9-[(1,1′-anhydro)-(2′,3′:4′,5′-di*-O-*isopropylidene-*D*-*gluco*-1′-yl)]}decalin **6-V″**‡*. ^1H NMR δ 6.01 (m, H-7), 5.81 (m, H-6), 4.62 (d, *J* 10.9, H-1′), ~4.1 (H-2), 3.91 (dd, $J_{3,4}$ 9.7, $J_{2,3}$ 10.0, H-3), 3.54 (dd, $J_{4,5}$ 10.8, H-4), 3.19 (dd, $J_{5,10}$ 6.8, $J_{9,10}$ 13.5, H-10), 2.80 (m, H-5), 2.34 (m, H-9), 2.28 and 2.07 (both H-8), 1.44, 1.42, 1.39 and 1.36 (2×*C*Me$_2$). ^{13}C NMR δ 162.5 (*C*OAr), 128.3 (C-7), 126.7 (C-6), 111.6 and 109.8 (2×*C*Me$_2$), 109.0 (C-1), 86.0 (C-2), 83.5 (C-3), 84.0 (C-4), 82.9 (C-1′), 78.0, 77.3 and 76.5 (C-2′,3′,4′), 76.1, 75.6 and 74.7 (3×OBn), 67.5 (C-5′), 47.1 (C-10), 38.6 (C-9), 38.1 (C-5), 27.2 (C-8), 27.1, 27.0, 26.7 and 25.2 (2×*C*Me$_2$). NOEs: H5–H10 (6%), H10–H11 (4.5%), H10–H11 (4.2%).

Under high pressure: High pressure reaction of **11a** with aldehyde **16** was unsuccessful; only traces of decalin **6a-V′** was isolated after 24 h under 10 kbar pressure.

4.8.2. Reaction of α-hydroxyaldehyde **16** with phosphonate **12a**

Aldehyde **16** (260 mg, 1 mmol) and phosphonate **12a** (680 mg, 1.2 mmol) were dissolved in anhydrous toluene (15 mL) to which potassium carbonate (0.5 g) and 18-crown-6 (ca. 30 mg) were added. The heterogeneous mixture was stirred at room temperature for 2 h, partitioned between ethyl acetate and brine, the organic layer was separated, washed with water, dried and concentrated and the product was purified as desribed above yielding decalin **6a-V′** (630 mg, 75%), which was converted into **6a-V″** (as in Section 4.8.1).

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‡ Although the systematic name of this compound coined by the C.A. service (not including stereochemistry) is: 4-nitro-benzoic acid 6,7,8-tris-benzyloxy-2-(2,2,2′,2′-tetramethyl-4,4′-bi-1,3-dioxolanyl-5-yl)-2a,5a,6,7,8,8b-hexahydro-2*H*,3*H*-naphtho-1,8-bc-furan-8a-yl ester, we named **6b-V″** by analogy to other decalins.

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