DOI: 10.1002/ejoc.201001443

Indium-Mediated Allenylation of Aldehydes and Its Application in Carbohydrate Chemistry: Efficient Synthesis of D-Ribulose and 1-Deoxy-D-ribulose

Michael Fischer,[a] Christoph Schmölzer,[a] Christina Nowikow,[a] and Walther Schmid*[a]

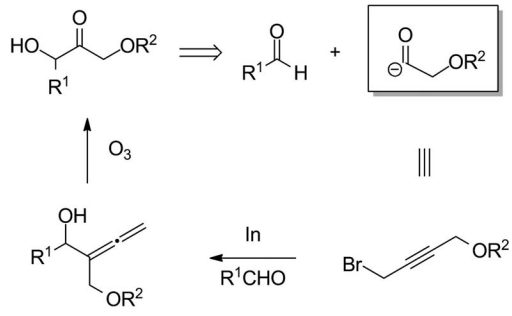
Keywords: Indium / Allenes / Carbohydrates / Acyl anion / Water chemistry

A two-step reaction sequence starting with the indium-mediated allenylation of aldehydes with 4-bromo-2-butyn-1-ols and subsequent ozonolysis of the resulting allenylic product was developed to generate a variety of dihydroxyacetone derivatives. The regioselectivity of the indium-promoted C–C bond-forming reaction can be manipulated through hydroxy protecting groups on 4-bromo-2-butyn-1-ol, yielding either allenes or alkynes as preferred products. Compared to established protocols, the necessary amount of indium for this type of allenylation can be decreased by a factor of two to four. The versatility of this strategy was demonstrated in the stereoselective and straightforward synthesis of D-ribulose and 1-deoxy-D-ribulose.

Introduction

Indium-mediated reactions, such as the addition of substituted propargyl bromides to aldehydes, have gained substantial interest in synthetic organic chemistry.[1,2] This reaction enables the regioselective formation of either homopropargylic or allenylic alcohols, the latter being extremely valuable synthetic intermediates due to their variability in chemical applications.[3] Suitably substituted propargyl bromides can be retrosynthetically seen as a source of α-hydroxyacetyl anion equivalents (Scheme 1), which play important roles in the concept of "umpolung" reactivity in synthetic strategies.[4] However, simple and mild methods for generating α-hydroxyacetyl anions are relatively scarce[5,6] although their application in the synthesis of a variety of natural products,[7] like cortical steroids, anthracycline antibiotics, or keto sugars, have impressively demonstrated their synthetic potential.

This publication reports on a facile synthetic sequence, generating an α-hydroxyacetyl anion equivalent from 4-bromo-2-butyn-1-ols and utilizing this synthon in an indium-mediated allenylation reaction of various aldehydes. The resulting allenes are converted into keto moieties by ozonolysis, thus forming the desired substituted dihydroxyacetone derivative. Because the regioselectivity of the indium-mediated reaction can be manipulated by the nature of the hydroxy protecting group of 4-bromo-2-butyn-1-ol, the ratio of the allene and alkyne products can be influenced within a certain range. We used this strategy for a stereoselective and efficient synthesis of D-*erythro*-2-pentulose (D-ribulose) and its 1-deoxy-D-*erythro*-2-pentulose analogue.



Scheme 1. Retrosynthetic concept.

Results and Discussion

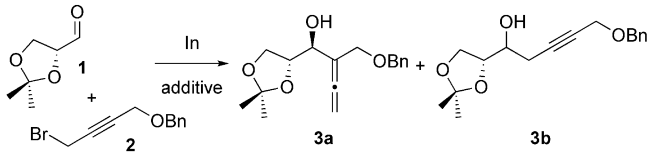
Our initial studies focused on the addition of 1-(benzyloxy)-4-bromo-2-butyne (**2**) to 2,3-*O*-isopropylidene-D-glyceraldehyde[8] (**1**) under indium promotion. Compound **1** was used as the starting aldehyde due to its synthetic importance as a starting material in carbohydrate chemistry and total syntheses.[9] The yields obtained are summarized in Table 1.

Reaction of **1** with the in situ generated organoindium reagent in water or THF did not yield significant amounts of products (Table 1, Entries 1 and 2).[10] In contrast, by addition of LiI or LiCl in THF the reaction proceeded smoothly and afforded good yields of desired allene **3a** (Table 1, Entries 3 and 8).[11,12] The use of THF/water mix-

[a] Department of Organic Chemistry, University of Vienna, Währingerstrasse 38, 1090 Vienna, Austria
Fax: +43-1-4277-9521
E-mail: walther.schmid@univie.ac.at

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001443.

Table 1. Indium-mediated reactions of 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**) with 1-(benzyloxy)-4-bromo-2-butyne (**2**).



1 + **2** → **3a** + **3b**

Entry[a]	Indium [equiv.]	Additive [equiv.]	Solvent	Yield [%][b]	**3a/3b**[c]
1	1.0		H_2O	0	nd
2	1.0		THF	ca. 5	nd
3	1.0	LiI (1.0)	THF	74	73:27
4	1.0	LiI (1.0)	THF/H_2O	58	52:48
5	1.0	LiI (3.0)	DMF	70	52:48
6	1.0	LiI (2.0)	THF	71	69:31
7	1.0	LiBr (2.0)	THF	46	70:30
8	1.0	LiCl (2.0)	THF	84	70:30
9	1.0	LiF (2.0)	THF	0	nd
10	0.55	LiI (1.0)	THF	69	78:22
11	0.55	LiCl (2.0)	THF	nd[d]	nd
12	1.0	*n*Bu_4NI (1.0)	THF	58	69:31
13	1.0	*n*Bu_4NCl (1.0)	THF	0	nd
14	1.0	$LiNO_3$ (2.0)	THF	0	nd
15	1.0	NaCl (2.0)	THF	35	68:32

[a] Except where indicated, all reactions were carried out on 0.5-mmol scale with aldehyde/bromide/indium = 1:1:1 under ultrasonic conditions. [b] Isolated combined yields of allenes and alkynes. [c] nd = not determined. [d] Starting materials were not fully consumed.

tures or DMF as solvent led to a decrease in the combined yields and regioselectivity (Table 1, Entries 4 and 5). The best results were obtained by addition of **1** to a suspension of indium (1 equiv.), propargyl bromide **2** (1 equiv.), and either LiI (1 equiv.) or LiCl (2 equiv.) in anhydrous THF under ultrasonic conditions (Table 1, Entries 3 and 8).[13] However, nearly half of the metallic indium remained unchanged in the reaction mixture after consumption of starting materials **1** and **2**.[14] Reducing the amount of indium to 0.55 equiv. resulted in nearly the same combined yields of allene **3a** and alkyne **3b** (Table 1, Entry 10), whereas the regioselectivity shifted towards desired allene **3a**. In this case, by substituting LiI with LiCl (Table 1, Entry 11) only trace amounts of products were observed. Additionally, a further decrease in the amount of indium to 0.2 equiv. led to incomplete consumption of starting materials **1** and **2**. For practical reasons, we used the optimized reaction conditions of Entry 10 (Table 1) for further studies.

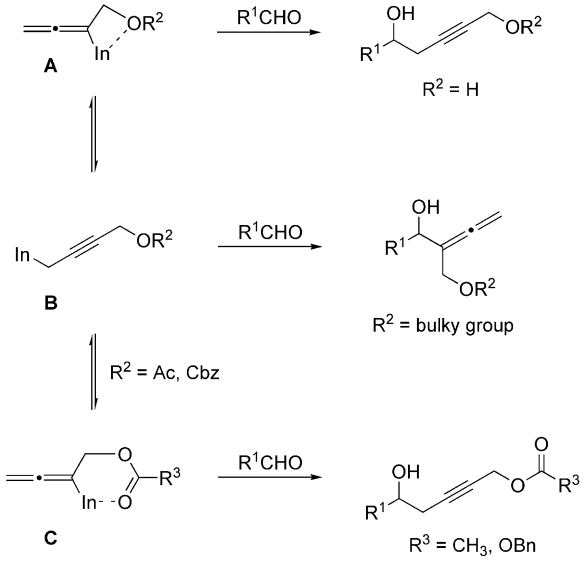
Interestingly, the allenylation of **1** was highly diastereoselective (>96%*de*), whereas the propargylation gave mixtures of diastereomers ranging from 4:1 to 2:1 (*erythro*/*threo*).[15] The configuration of the stereocenter formed in product **3a** was unambiguously assigned by transformation of the allenylic alcohol into the corresponding D-*erythro*-2-pentulose (**25**).[16] The observed *anti* relationship between the newly generated hydroxy group and the C2 hydroxy group of starting aldehyde **1** can be easily rationalized by the Felkin–Anh model.[17]

The organoindium species involved in this type of reaction was the subject of numerous investigations.[18,19] The data summarized in Table 1 suggest some basic mechanistic considerations. In general, propargyl iodides proved to be more reactive than bromides, albeit leading to lower yields.[20] The addition of LiI to the reaction mixtures accelerated the formation of the reactive organoindium species, presumably by in situ generation of the corresponding propargyl iodides.[21] The addition of LiCl instead of LiI beneficially influenced the combined yield of alkyne- and allene-type products (Table 1, Entries 6 and 8).[22] However, only in the case where LiI was applied could the amount of indium be decreased significantly (Table 1, Entries 10 and 11). Using tetrabutylammonium salts instead of lithium salts only in the case of *n*Bu_4NI led to product formation (Table 1, Entries 12 and 13).[23] In general, Grignard-type reaction conditions were superior to Barbier-type ones.[12b]

Because indium chelates to oxygen functionalities,[24] we hypothesized that the hydroxy protecting group of compound **2** is crucial for the regioselective formation of **3a** and **3b** (Scheme 2).[25] The results are summarized in Table 2. In analogy to the investigations of Lin et al. on siliconated propargyl bromides,[2a] we observed that bulky protecting groups favor the formation of the allenylic alcohols (i.e., **3a** and **8a**; Table 2, Entries 1 and 6) presumably via intermediate **B** (Scheme 2). As expected, changing the protecting group from benzyl to methyl decreased the regioselectivity for the formation of **4a** while increasing the combined yield (Table 2, Entry 2). Unprotected 4-bromo-2-butyn-1-ol (**5**; Table 2, Entry 3) reversed the regioselectivity of the reaction presumably by formation of intermediate **A** (Scheme 2), thus yielding mainly homopropargylic alcohol **5b**. In addition, acetyl- or Cbz-protected 4-bromo-2-butyn-1-ol may stabilize allenylic intermediate **C** by formation of a six-membered transition state, thus yielding propargylic derivatives (i.e., **6b** and **7b**; Table 2, Entries 4 and 5) preferentially. Further evidence for intermediate **C** was obtained by the following observations: Compounds with an oxygen atom too distant for chelating the allenylic intermediate or lacking an oxygen atom (Table 2, Entries 7 and 8) almost exclusively gave allenylic products **9a** and **10a**.

These results led us to examine the relative reactivity of 1-(benzyloxy)-4-bromo-2-butyne (**2**) towards a variety of different aldehydes (Table 3). In summary, citronellal gave lower yields than aromatic and α,β-unsaturated aldehydes (Table 3, Entries 1–4). 2-Phenylpropionaldehyde and the serine-derived "Garner aldehyde" gave good to excellent diastereoselectivity (Table 3, Entries 5 and 6).[26] As observed for 4-hydroxybenzaldehyde, a free hydroxy group is tolerated in carbonyl substrates (Table 3, Entry 3).

Furthermore, we examined the potential reactivity of 1-(benzyloxy)-4-bromo-2-butyne (**2**) towards water-soluble substrates (Table 3, Entries 7–11). In these cases, we added an aqueous solution of the corresponding aldehydes to the preformed indium intermediate, resulting in THF/water mixtures of 2:1. As depicted in Table 3, a freshly prepared solution of formaldehyde reacted smoothly with **2**, yielding compound **17a** in excellent yield. In analogy, aqueous solu-



Scheme 2. Allenylation vs. propargylation: influence of hydroxy protecting groups on regioselectivity. The corresponding organoindium(III) species are not shown.[19]

Table 2. Indium-mediated reactions of 2,3-*O*-isopropyliden-D-glyceraldehyde (**1**) with substituted propargyl bromides.

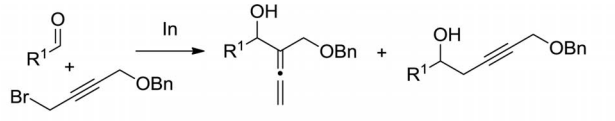
Entry[a]	$BrCH_2CCR^1$, R^1 =	Yield [%][b]	Allene/Alkyne
1	CH_2OCH_2Bn (**2**)	69	78:22 (**3a/3b**)
2	CH_2OCH_3 (**4**)	80	60:40 (**4a/4b**)
3	CH_2OH (**5**)	70	28:72 (**5a/5b**)
4	CH_2OAc (**6**)	70	45:55 (**6a/6b**)[c]
5	CH_2OCbz (**7**)	65	49:51 (**7a/7b**)
6	$CH_2OTBDPS$ (**8**)	48	67:33 (**8a/8b**)
7	CH_3 (**9**)	75	98:2 (**9a/9b**)
8	$CCCH_2OH$ (**10**)	40	>99:1 (**10a/10b**)

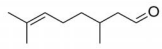
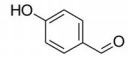
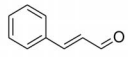
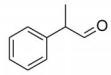
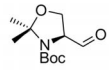
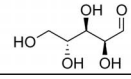
[a] All reactions were carried out on 0.5-mmol scale with aldehyde/bromide/LiI/indium = 1:1:1:0.55 under ultrasonic conditions. [b] Isolated combined yield. [c] Partial acetyl migration in allenylic product **6a** was observed (1-OAc/3-OAc = 56:44).

tions of glycolaldehyde and chloroacetaldehyde were used and again satisfactory yields were obtained (Table 3, Entries 8 and 9). With unprotected D-glyceraldehyde, the *syn* allenylation product was obtained in high diastereoselectivity (Table 3, Entry 10).[27] Unprotected D-arabinose produced an inseparable mixture of corresponding allene **21a** and alkyne **21b** in low yield (Table 3, Entry 11).[28] The change in regioselectivity of Garner's aldehyde and D-glyceraldehyde (Table 3, Entries 6 and 10) in comparison to the other aldehydes used is remarkable, although we do not have a satisfactory explanation of this phenomenon at the moment.

Subsequently, as proof of concept for the present methodology, allene **3a** was converted into corresponding pentulose **25** (Scheme 3). Ozonolysis of the allene functionality of **3a** at –78 °C in dichloromethane gave 2-keto derivative **22** in excellent yield. Deprotection of the benzyl and acetonide protecting groups was achieved by standard procedures to yield D-*erythro*-2-pentulose (**25**).[29]

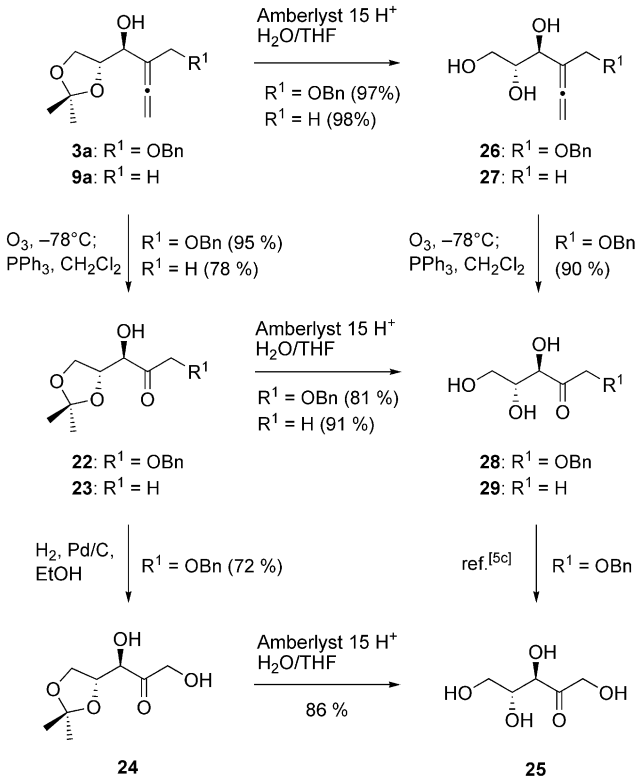
Table 3. Indium-mediated allenylation of aldehydes with 1-(benzyloxy)-4-bromo-2-butyne (**2**).



Entry[a]	Aldehyde [equiv.]	Indium [equiv.]	Yield [%][b]	Allene/Alkyne[d]
1		0.55	58	78:22 (**11a/11b**)
2		0.55	90	76:24 (**12a/12b**)
3		0.55	60	76:24 (**13a/13b**)
4		0.55	88[c]	78:22 (**14a/14b**)[e]
5		0.55	83	70:30 (**15a/15b**)
6		1	77[c]	35:65 (**16a**:**16b**)
7		0.66	87	74:26 (**17a/17b**)
8		0.55	86	61:39 (**18a/18b**)
9		0.55	58	83:17 (**19a/19b**)[f]
10		1	53	38:62 (**20a/20b**)
11		1	5	50:50 (**21a/21b**)[g]

[a] Except where indicated, all reactions were carried out on 1.0-mmol scale with aldehyde/bromide/LiI = 1:1:1 under ultrasonic conditions. Solvents: THF (Entries 1–6), THF/H_2O = 2:1 (Entries 7–11). [b] Isolated combined yield. [c] Yield is adjusted to account for recovered starting materials. [d] Diastereomeric ratios of allenylic products (*anti*/*syn*): **15a** (1:10), **16a** (40:1), **20a** (1:8), and **21a** (1:20). [e] Cinnamyl aldehyde only gave regiospecific 1,2-addition products. [f] Chloride was substituted by iodide in a ratio of 1:3 in the allenylic products. [g] Instead of LiI, LiCl (2 equiv.) was used.

The versatility of the present methodology was further demonstrated by an efficient synthesis of 1-deoxy-D-ribulose (**29**).[30,31] In a three-step synthesis, **29** was obtained in an overall yield of 51% starting from **1** and by using 1-bromo-2-butyne as an acetyl anion equivalent.[32] In comparison to the literature,[33] when adding LiI the applied quantities of 1-bromo-2-butyne and indium were decreased by a factor of two and four, respectively. Because **3a** is a fully orthogonally protected precursor, the sequence of deprotection steps can be easily altered, giving rise to various derivatives of pentulose (**24**, **26**, and **28**).



Scheme 3. Synthesis of D-*erythro*-2-pentulose (**25**) and 1-deoxy-D-*erythro*-2-pentulose (**29**).

Conclusions

Hydroxy-protected 4-bromo-2-butyn-1-ols (i.e., **2**, **4**, **6**–**8**) are versatile synthetic equivalents for α-hydroxyacetyl anions. This fact is demonstrated by their application in a short and efficient indium-mediated synthesis of D-*erythro*-2-pentulose (**25**) in 32% overall yield. The regioselectivity of the indium-promoted C–C bond-forming reaction can be influenced by the protecting group on 4-bromo-2-butyn-1-ol (for **2**, **4**–**8**). Due to chelation control, the addition of unprotected 4-bromo-2-butyn-1-ol (**5**) to aldehydes yields mainly alkyne-type products, whereas the addition of 1-(benzyloxy)-4-bromo-2-butyne (**2**) leads to allene-type derivatives preferentially. Compared to established synthetic protocols, the amount of indium was decreased by a factor of two to four. Furthermore, the reaction presented tolerates aqueous reaction conditions, thus significantly broadening the scope of this method. The applicability of this concept is further demonstrated by a three-step synthesis of 1-deoxy-D-*erythro*-2-pentulose (**29**).

Experimental Section

General Considerations: All allenylations were carried out in oven-dried Erlenmeyer flasks under an argon atmosphere. Ultrasonication was performed in a conventional ultrasound cleaning bath at room temperature. Indium (powder, 100 mesh) was purchased by Sigma–Aldrich. Anhydrous THF was distilled from potassium under an atmosphere of argon. ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker Avance DRX 400 MHz or DRX 600 MHz spectrometer. Unless otherwise stated, all NMR spectra were measured either in $CDCl_3$ solutions and referenced to the residual $CHCl_3$ signal (^{1}H, δ = 7.26 ppm; ^{13}C, δ = 77.16 ppm) or in D_2O solutions (HDO, ^{1}H, δ = 4.79 ppm). High-resolution mass spectrometry (HRMS) was performed with a Finnigan MAT 900 with resolution of 10000. Optical rotations were measured with a P341 Perkin–Elmer polarimeter. Flash chromatography was performed by using Merck silica gel 60 (0.004–0.063 mm). TLC monitoring was done on Merck plates (silica gel 60 F_{254}), and compounds were visualized by treatment with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (48 g) and $Ce(SO_4)_2$ (2 g) in 10% H_2SO_4 (1 L), followed by heating, or with an aqueous $KMnO_4$ solution. 2,3-*O*-Isopropylidene-D-glyceraldehyde and *O*-protected 4-bromobut-2-yn-1-ol were prepared by following literature procedures.[8,25] For the preparation of the formalin solution, paraformaldehyde (1.08 g, 36 mmol) was heated at reflux in water (20 mL) containing concentrated H_3PO_4 (200 μL) for 1.5 h until a clear solution was obtained.

Standard Conditions for Allenylation (Method A): Synthesis of Compounds 3a–21a and 3b–21b

Representative Procedure of the Reaction of Aldehydes with Indium and Substituted Propargyl Bromides: To a suspension of powdered indium (32 mg, 0.275 mmol) and LiI (67 mg, 0.5 mmol) in dry THF (4 mL) was added 1-(benzyloxy)-4-bromo-2-butyne (**2**; 120 mg, 0.5 mmol). After the mixture was sonicated for 20 min under an argon -atmosphere, 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**; 65 mg, 0.5 mmol) was added. The reaction mixture was further sonicated until TLC monitoring (hexane/ethyl acetate = 3:2) showed complete consumption of the starting material. The reaction was quenched by the addition of a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was separated and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with thiosulfate solution (2%) and brine, dried with $MgSO_4$, filtered, and concentrated. The regioisomers were separated by silica gel column chromatography (hexane/ethyl acetate = 5:1) to yield **3a** (78 mg, 54%) and **3b** (22 mg, 15%). The yield of the reaction was not decreased by scaling up to 2 mmol.

1-*O*-Benzyl-2-deoxy-2-*C*-ethenylidene-4,5-*O*-isopropylidene-D-*erythro*-pentitol (3a): $[\alpha]_D^{20}$ = +20.2 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 5 H, Ar-H), 4.97–4.93 (m, 2 H, CH_2), 4.56 (d, ^2J = 11.9 Hz, 1 H, CH_2), 4.53 (d, ^2J = 11.9 Hz, 1 H, CH_2), 4.36–4.30 (m, 1 H, CH), 4.26 (dt, ^2J = 11.3 Hz, ^5J = 2.2 Hz, 1 H, CH_2), 4.22 (m, 1 H, CH), 4.14 (dt, ^2J = 11.3 Hz, ^5J = 1.8 Hz, 1 H, CH_2), 4.05 (dd, ^2J = 8.4 Hz, ^3J = 6.3 Hz, 1 H, CH_2), 4.01 (dd, ^2J = 8.4 Hz, ^3J = 6.1 Hz, 1 H, CH_2), 2.64 (d, ^3J = 4.4 Hz, 1 H, OH), 1.43 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 207.2 (C), 137.8 (C), 128.6 (2 CH), 128.1 (2 CH), 128.0 (CH), 109.4 (C), 100.4 (C), 77.9 (CH_2), 77.5 (CH), 72.5 (CH_2), 71.2 (CH), 69.8 (CH_2), 65.8 (CH_2), 26.7 (CH_3), 25.3 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3433, 2931, 1957, 1062, 738, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{22}O_4Na$ $[M + Na]^+$ 313.1416; found 313.1411.

(2*R*)-7-(Benzyloxy)-1,2-*O*-isopropylidenehept-5-yne-1,2,3-triol (3b): Mixture of two diastereomers: major/minor = 2.8:1.0. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 7.37–7.27 (m, 5 H, Ar-H), 4.59 (s, 2 H, CH_2), 4.19–4.15 (m, 2 H, CH_2), 4.11–4.04 (m, 2 H, CH_2), 4.01–3.94 (m, 1 H, CH), 3.80–3.74 (m, 1 H, CH), 2.63–2.48 (m, 2 H, CH_2), 1.42 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, major isomer): δ = 137.6 (C), 128.6 (2 CH), 128.2 (2 CH), 128.0 (CH), 109.5 (C), 82.3 (C), 79.2 (C), 77.5 (CH), 71.9 (CH_2), 70.4 (CH), 66.0 (CH_2), 57.8 (CH_2), 26.8 (CH_3), 25.3 (CH_3), 24.1 (CH_2) ppm. IR (film): $\tilde{\nu}$ = 3377, 2825, 2240, 1062, 747. 699 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{22}O_4Na$ $[M + Na]^+$ 313.1416; found 313.1406.

Typical Procedure for Ozonolysis (Method B): Synthesis of Compounds 22, 23, and 28

1-*O*-Benzyl-4,5-*O*-isopropylidene-D-*erythro*-2-pentulose (22): Ozone was bubbled through a solution of compound **3a** (145 mg, 0.5 mmol) in CH_2Cl_2 (25 mL) at –78 °C until the color of the mixture turned blue. Dry air was bubbled through the solution until the blue color disappeared. After addition of PPh_3 (157 mg, 0.6 mmol), the mixture was allowed to reach room temperature by stirring overnight. The solvent was removed under reduced pressure, and the crude material was purified by flash chromatography (hexane/ethyl acetate = 4:1) to yield compound **22** (133 mg; 95%). $[\alpha]_D^{20}$ = –57.3 (*c* = 0.3, CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 5 H, Ar-H), 4.62 (s, 2 H, CH_2), 4.57 (d, ^2J = 18.2 Hz, 1 H, CH_2), 4.29 (d, ^2J = 17.9 Hz, 1 H, CH_2), 4.17 (dd, ^2J = 6.7 Hz, ^3J = 6.4 Hz, 1 H, CH_2), 4.12–3.93 (m, 3 H, 2 CH, CH_2), 3.29 (d, ^3J = 5.8 Hz, 1 H, OH), 1.42 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 208.0 (C), 137.1 (C), 128.7 (2 CH), 128.3 (CH), 128.2 (2 CH), 110.4 (C), 76.2 (CH), 75.3 (CH), 73.7 (CH_2), 73.6 (CH_2), 67.1 (CH_2), 26.7 (CH_3), 25.2 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3386, 2934, 1729, 1067, 739, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_5Na$ $[M + Na]^+$ 303.1208; found 303.1206.

1-Deoxy-4,5-*O*-isopropylidene-D-*erythro*-2-pentulose (23): Method B was applied to compound **9a** (92 mg, 0.5 mmol) for ozonolysis to yield product **23** (68 mg; 78%). $[\alpha]_D^{20}$ = –90.6 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.14–4.01 (m, 3 H, CH CH_2), 3.95–3.87 (m, 1 H, CH), 3.47 (d, ^3J = 5.4 Hz, 1 H, OH), 2.3 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 209.1 (C), 110.4 (C), 77.6 (CH), 76.4 (CH), 67.5 (CH_2), 27.7 (CH_3), 26.8 (CH_3), 25.4 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3424, 2989, 1716, 1069 cm^{-1}. HRMS (ESI): calcd. for $C_8H_{14}O_4Na$ $[M + Na]^+$ 197.0790; found 197.0794.

4,5-*O*-Isopropylidene-D-*erythro*-2-pentulose (24): Pentulose derivative **22** (21 mg, 0.075 mmol) was dissolved in ethanol (2 mL) and hydrogenated in the presence of 10% palladium-on-charcoal (1 mg) with a balloon of hydrogen. The catalyst was removed by filtration, and the solvent was removed under reduced pressure to yield compound **24** (10 mg, 72%). $[\alpha]_D^{20}$ = –71.5 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.68 (dd, ^2J = 20.1 Hz, ^3J = 5.0 Hz, 1 H, CH_2), 4.40 (dd, ^2J = 20.0 Hz, ^3J = 3.5 Hz, 1 H, CH_2), 4.24 (dd, ^3J = 7.7 Hz, ^3J = 5.2 Hz, 1 H, CH), 4.14 (dd, ^2J = 8.9 Hz, ^3J = 6.3 Hz, 1 H, CH_2), 4.07 (dd, ^2J = 8.9 Hz, ^3J = 5.0 Hz, 1 H, CH_2), 3.99 (ddd, ^3J = 7.8 Hz, ^3J = 6.3 Hz, ^3J = 5.1 Hz, 1 H, CH), 3.24 (d, ^3J = 5.4 Hz, 1 H, OH), 3.05 (t, ^3J = 4.9 Hz, 1 H, OH), 1.49 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 210.7 (C), 110.6 (C), 76.0 (CH), 75.4 (CH), 67.6 (CH_2), 67.3 (CH_2), 26.7 (CH_3), 25.1 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3411, 2925, 1726, 1066 cm^{-1}. HRMS (EI): calcd. for $C_7H_{11}O_6$ $[M - CH_3]^+$ 175.0606; found 175.0610.

Typical Procedure for Isopropylidine Cleavage of Ketoses (Method C): Synthesis of Compounds 25, 28, and 29

D-*erythro*-2-Pentulose (25): To a suspension of 4,5-*O*-isopropylidene-D-*erythro*-2-pentulose (**24**; 9 mg, 0.047 mmol) in water/THF (1:1, 0.8 mL) was added Amberlyst 15 (H^+ form, 6 mg), and the mixture was stirred at room temperature. After TLC monitoring showed conversion of the starting material, the pH of the solution was adjusted to 7 by addition of 0.05 N NaOH. The resin was removed by filtration and washed with water, and the solvent was lyophilized. The crude product was purified by flash chromatography over silica gel (ethyl acetate/MeOH = 8:1) to yield **25** (6.1 mg, 86%). Equilibrium of three compounds: α/β/open = 58:24:18. $[\alpha]_D^{20}$ = –14.0 (*c* = 0.25, H_2O). The spectroscopic data were identical with those reported.[16]

Typical Procedure for Isopropylidine Cleavage of Allenes (Method D): Synthesis of Compounds 26 and 27

1-*O*-Benzyl-2-deoxy-2-*C*-ethenylidene-D-*erythro*-pentitol (26): To a suspension of compound **3a** (34 mg, 0.117 mmol) in water/THF (1:1, 2 mL) was added Amberlyst 15 (H^+ form, 40 mg), and the mixture was stirred at room temperature. After TLC monitoring showed conversion of the starting material, the resin was removed by filtration and washed with methanol, and the solvent was removed under reduced pressure to yield compound **26** (28 mg; 97%). $[\alpha]_D^{20}$ = +14.8 (*c* = 0.25, MeOH). ^{1}H NMR (400 MHz, D_2O): δ = 7.58–7.36 (m, 5 H, Ar-H), 5.12 (s, 2 H, CH_2), 4.64 (s, 2 H, CH_2), 4.27–4.13 (m, 3 H, CH, CH_2), 3.89–3.77 (m, 2 H, CH_2), 3.73–3.61 (m, 1 H, CH_2) ppm. ^{13}C NMR (400 MHz, D_2O): δ = 207.0 (C), 137.1 (C), 128.8 (2 CH), 128.7 (2 CH), 128.4 (CH), 100.4 (C), 78.7 (CH_2), 73.2 (CH), 71.8 (CH_2), 70.5 (CH), 67.9 (CH_2), 62.5 (CH_2) ppm. IR (film): $\tilde{\nu}$ = 3377, 2926, 1956, 1055, 745, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}O_4Na$ $[M + Na]^+$ 273.1103; found 273.1099.

(2*R*,3*S*)-4-Methylhexa-4,5-dien-1,2,3-triol (27): Method D was applied to compound **9a** (46 mg, 0.25 mmol) for deprotection to yield product **27** (35 mg, 98%). $[\alpha]_D^{20}$ = +25.9 (*c* = 0.35, MeOH). ^{1}H NMR (400 MHz, D_2O): δ = 4.88–4.80 (m, 2 H, CH_2), 4.08 (dt, ^3J = 7.5 Hz, ^5J = 1.4 Hz, 1 H, CH), 3.85 (dd, ^2J = 11.7 Hz, ^3J = 2.78 Hz, 1 H, CH_2), 3.81–3.74 (m, 1 H, CH), 3.66 (dd, ^2J = 11.7 Hz, ^3J = 6.6 Hz, 1 H, CH_2), 1.75 (t, ^5J = 3.22 Hz, 3 H, CH_3) ppm. ^{13}C NMR (600 MHz, D_2O): δ = 206.9 (C), 98.5 (C), 76.0 (CH_2), 73.4 (CH), 72.7 (CH), 63.0 (CH_2), 14.0 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3317, 2926, 1961, 1035 cm^{-1}. HRMS (ESI): calcd. for $C_7H_{12}O_3Na$ $[M + Na]^+$ 167.0684; found 167.0680.

1-*O*-Benzyl-D-*erythro*-2-pentulose (28): Method C was applied to compound **22** (39 mg, 0.139 mmol) for deprotection to yield product **28** (27 mg; 81%), or compound **26** (25 mg, 0.1 mmol) was ozonized in a mixture of MeOH/CH_2Cl_2 (9:1) according to method B to yield product **28** (21.6 mg; 90%). Equilibrium of three compounds: α/β/open = 62:25:13. $[\alpha]_D^{20}$ = –20.7 (*c* = 2.25, MeOH). ^{1}H NMR (600 MHz, CD_3COCD_3+D_2O, α-isomer): δ = 7.39–7.23 (m, 5 H, Ar-H), 4.65–4.46 (m, 2 H, CH_2), 4.22–4.17 (m, 1 H, CH), 4.06 (d, ^3J = 5.3 Hz, 1 H, CH), 3.92 (dd, ^2J = 9.4 Hz, ^3J = 5.3 Hz, 1 H, CH_2), 3.78 (dd, ^2J = 9.3 Hz, ^3J = 3.6 Hz, 1 H, CH_2), 3.52 (d, ^2J = 10.6 Hz, 1 H, CH_2), 3.44 (d, ^2J = 10.2 Hz, 1 H, CH_2) ppm. ^{1}H NMR (600 MHz, CD_3COCD_3+D_2O, β-isomer): δ = 7.39–7.23 (m, 5 H, Ar-H), 4.65–4.46 (m, 2 H, CH_2), 4.45–4.38 (m, 1 H, CH), 4.04 (dd, ^2J = 8.9 Hz, ^3J = 6.3 Hz, 1 H, CH_2), 3.97 (d, ^3J = 5.3 Hz, 1 H, CH), 3.71 (d, ^2J = 10.2 Hz, 1 H, CH_2), 3.64 (dd, ^2J = 8.9 Hz, ^3J = 4.7 Hz, 1 H, CH_2), 3.58 (d, ^2J = 10.2 Hz, 1 H, CH_2) ppm. ^{1}H NMR (600 MHz, CD_3COCD_3+D_2O, open isomer): δ = 7.71–7.55 (m, 2 H, Ar-H), 7.64–7.60 (m, 1 H, Ar-H), 7.57–7.51 (m, 2 H, Ar-H), 4.65–4.46 (m, 4 H, 2 CH_2), 4.23 (d, ^3J = 5.7 Hz, 1 H, CH), 3.89–3.84 (m, 1 H, CH), 3.66 (dd, ^2J = 11.0 Hz, ^3J = 5.3 Hz, 1 H, CH_2), 3.59 (dd, ^2J = 11.2 Hz, ^3J = 5.9 Hz, 1 H, CH_2) ppm. ^{13}C NMR (600 MHz, CD_3COCD_3+D_2O, α-isomer): δ = 139.3 (C), 129.0 (2 CH), 128.2 (2 CH), 128.1 (CH), 103.3 (C), 73.8 (CH_2), 72.2 (CH_2), 71.9 (CH_2), 71.8 (CH), 71.2 (CH) ppm. ^{13}C NMR (600 MHz, CD_3COCD_3+D_2O, β-isomer): δ = 139.2 (C), 128.5 (CH), 128.4 (2 CH), 128.1 (2 CH), 106.1 (C), 76.9 (CH), 74.0 (CH_2), 72.3 (CH_2), 71.9 (CH_2), 71.6 (CH) ppm. ^{13}C NMR (600 MHz, CD_3COCD_3+D_2O, open isomer): δ = 209.7 (C), 139.5 (C), 132.9 (2 CH), 132.6 (2 CH), 132.5 (CH), 77.0 (CH), 74.4 (CH_2), 74.2 (CH), 73.3 (CH_2), 62.9 (CH_2) ppm. HRMS (ESI): calcd. for $C_{12}H_{16}O_5Na$ $[M + Na]^+$ 263.0895; found 263.0893.

1-Deoxy-D-*erythro*-2-pentulose (29): Method C was applied to compound **23** (10 mg, 0.057 mmol) for deprotection to yield product **29** (7 mg; 91%). Equilibrium of three compounds: α/β/open =

14:14:72. $[a]_D^{20}$ = –30 (c = 0.3, H_2O). The spectroscopic data were identical with those reported.[30,31] HRMS (ESI): calcd. for $C_5H_9O_4$ $[M – H]^-$ 133.0501; found 133.0504. HRMS (EI): calcd. for $C_5H_8O_3$ $[M – H_2O]^+$ 116.0473; found 116.0476.

Supporting Information (see footnote on the first page of this article): Experimental and spectroscopic details for compounds **6**–**8**, **10**, **4a**–**21a**, **4b**–**21b**, **30a**, **30b**, **31a**, and **31b** and ^1H and ^{13}C NMR spectra of compounds **6**–**8**, **10**, **22**–**29**, **3a**, **3b**, **4a**–**21a**, **21b**, **30a**, **30b**, **31a**, and **31b**.

Acknowledgments

We thank Dr. Hanspeter Kählig, Dr. Lothar Brecker, Susanne Felsinger, and Peter Unteregger, University of Vienna, for NMR and MS measurements.

[1] Recent review articles: a) J. Augé, N. Lubin-Germain, J. Uziel, *Synthesis* **2007**, 1739–1764; b) S. Araki, T. Hirashita, *Comp. Organomet. Chem. III* **2007**, *9*, 649–751; c) C.-J. Li, *Chem. Rev.* **2005**, *105*, 3095–3165.

[2] a) M.-J. Lin, T.-P. Loh, *J. Am. Chem. Soc.* **2003**, *125*, 13042–13043; b) T.-P. Loh, M.-J. Lin, K.-L. Tan, *Tetrahedron Lett.* **2003**, *44*, 507–509; c) W. Miao, W. Lu, T. H. Chan, *J. Am. Chem. Soc.* **2003**, *125*, 2412–2413; d) P. H. Lee, H. Kim, K. Lee, M. Kim, K. Noh, H. Kim, D. Seomoon, *Angew. Chem. Int. Ed.* **2005**, *44*, 1840–1843; e) Z. Wang, G. B. Hammond, *J. Org. Chem.* **2000**, *65*, 6547–6552; f) B. Alcaide, P. Almendros, C. Aragoncillo, *Org. Lett.* **2000**, *2*, 1411–1414; g) J.-M. Huang, H.-C. Luo, Z.-X. Chen, G.-C. Yang, T.-P. Loh, *Eur. J. Org. Chem.* **2008**, *2*, 295–298; h) K. Lee, H. Kim, T. Miura, K. Kiyoka, H. Kusama, S. Kim, N. Iwasawa, P. H. Lee, *J. Am. Chem. Soc.* **2003**, *125*, 9682–9688; i) see ref.[10,12,22,27,33]

[3] a) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701–712; b) N. Krause, A. Hoffmann-Röder, J. Canisius, *Synthesis* **2002**, 1759–1774; c) M. A. Tius, *Science Synthesis* **2007**, *44*, 353–394; d) N. Krause, A. S. K. Hashmi, *Modern Allene Chemistry*, Wiley-VCH, Weinheim, **2004**; e) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067–3126.

[4] a) D. Seebach, *Angew. Chem.* **1979**, *91*, 259–278; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239–258; b) R. Brehme, D. Enders, R. Fernandez, J. M. Lassaletta, *Eur. J. Org. Chem.* **2007**, 5629–5660; c) T. A. Hase, *Umpoled Synthons*, Wiley, New York, **1987**; d) J. S. Johnson, *Angew. Chem. Int. Ed.* **2004**, *43*, 1326–1328; e) M. Yus, C. Nájera, F. Foubelo, *Tetrahedron* **2003**, *59*, 6147–6212.

[5] Chemical synthesis: a) K. Suzuki, Y. Yuki, T. Mukaiyama, *Chem. Lett.* **1981**, 1529–1532; b) M. Fetizon, P. Goulaouic, I. Hanna, *Tetrahedron Lett.* **1985**, *26*, 4925–4928; c) M. Murakami, T. Kawano, Y. Ito, *J. Am. Chem. Soc.* **1990**, *112*, 2437–2439; d) M. Murakami, T. Kawano, H. Ito, Y. Ito, *J. Org. Chem.* **1993**, *58*, 1458–1465; e) H. Paulsen, K. Roden, V. Sinnwell, P. Luger, *Liebigs Ann. Chem.* **1981**, *11*, 2009–2027; f) J. Cheng, Z. Fang, S. Li, B. Zheng, Y. Jiang, *Carbohydr. Res.* **2009**, *334*, 2093–2095; g) M. E. B. Smith, K. Smithies, T. Senussi, P. A. Dalby, H. C. Hailes, *Eur. J. Org. Chem.* **2006**, 1121–1123; h) J. C. Swoden, D. R. Strobach, *J. Am. Chem. Soc.* **1958**, *80*, 2532–2533.

[6] Enzymatic synthesis: a) J. Bolte, C. Demuynck, H. Samaki, *Tetrahedron Lett.* **1987**, *28*, 5525–5528; b) Y. Kobori, D. C. Myles, G. M. Whitesides, *J. Org. Chem.* **1992**, *57*, 5899–5907; c) T. Ziegler, A. Straub, F. Effenberger, *Angew. Chem.* **1988**, *100*, 737–738; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 716–717; d) A. J. Humphrey, S. F. Parsons, M. E. B. Smith, N. J. Turner, *Tetrahedron Lett.* **2000**, *41*, 4481–4485.

[7] a) Z. J. Witczak in *Glycoscience: Vol. 2* (Eds.: B. O. Fraser-Reid, L. Tatsuta, J. Thiem), Springer, Berlin, **2008**, pp. 815–840; b) Sir D. H. R. Barton, K. Nakanishi, O. Meth-Cohn (Eds.), *Comprehensive Natural Products Chemistry*, Elsevier Science Ltd., Amsterdam, **1999**, vols. 2 & 4.

[8] L. W. Hertel, C. S. Grossman, J. S. Kroin, *Synth. Commun.* **1991**, *21*, 151–154.

[9] a) P. Vogel, *The Organic Chemistry of Sugars* (Eds.: D. E. Levy, P. Fügedi), Taylor & Francis, Boca Raton, **2006**, pp. 629–725; b) J. Jurczak, S. Pikul, T. Bauer, *Tetrahedron* **1986**, *42*, 447–488; c) J. Mulzer, *Org. Synth. Highlights* **1991**, 243–250.

[10] a) M. B. Isaac, T.-H. Chan, *J. Chem. Soc., Chem. Commun.* **1995**, 1003–1004; b) W. Lu, J. Ma, Y. Yang, T.-H. Chan, *Org. Lett.* **2000**, *2*, 3469–3471.

[11] Use of LiI in indium-mediated allylation of aldehydes: S. Araki, H. Ito, Y. Butsugan, *J. Org. Chem.* **1988**, *53*, 1831–1833.

[12] Use of LiI in indium-mediated allenylation of aldehydes: a) S. Kim, K. Lee, D. Seomoon, P. H. Lee, *Adv. Synth. Catal.* **2007**, *349*, 2449–2453; b) C. Park, P. H. Lee, *Org. Lett.* **2008**, *10*, 3359–3362; c) J. Park, S. H. Kim, P. H. Lee, *Org. Lett.* **2008**, *10*, 5067–5070.

[13] K. S. Suslik (Ed.), *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH Publishers, New York, **1988**.

[14] Similar observations were reported by Hammond et al. in studies of difluoroalkynyl bromide with indium in a THF/water mixture (see ref.[2e]).

[15] Diastereoselectivities were determined by ^1H NMR spectroscopy. No diastereomer of **3a** was detected.

[16] ^1HNMR, ^{13}C NMR, and HRMS data were in full agreement with previously published data: a) T. Vuorinen, A. S. Serianni, *Carbohydr. Res.* **1990**, *209*, 13–31; b) D. de Wit, F. van Rantwijk, L. Maat, A. P. G. Kieboom, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 271–274.

[17] B. Alcaide, P. Almendros, T. Martínez del Campo, E. Sorinao, J. L. Marco-Contelles, *Chem. Eur. J.* **2009**, *15*, 9127–9138.

[18] Allylindium systems: a) K. Koszinowski, *J. Am. Chem. Soc.* **2010**, *132*, 6032–6040; b) M. Yasuda, M. Haga, Y. Nagaoka, A. Baba, *Eur. J. Org. Chem.* **2010**, 5359–5363; c) M. Yasuda, M. Haga, A. Baba, *Eur. J. Org. Chem.* **2009**, 5513–5517; d) T. H. Chan, Y. Yang, *J. Am. Chem. Soc.* **1999**, *121*, 3228–3229; e) Ref. 11.

[19] Propargyl–allenylindium system: a) W. Miao, L. W. Chung, Y.-D. Wu, T.-H. Chan, *J. Am. Chem. Soc.* **2004**, *126*, 13326–13334; b) B. Xu, G. B. Hammond, *Chem. Eur. J.* **2008**, *14*, 10029–10035; c) B. Xu, M. S. Mashuta, G. B. Hammond, *Angew. Chem. Int. Ed.* **2006**, *45*, 7265–7267.

[20] Allenylation of benzaldehyde with 1-(benzyloxy)-4-iodobut-2-yne gave the corresponding allene and alkyne in a combined yield of 76% compared to 90% with 1-(benzyloxy)-4-bromo-2-butyne (**2**). In the case of 1-(benzyloxy)-4-iodo-2-butyne, the self-coupling product could be isolated. Furthermore 1-(benzyloxy)-4-iodo-2-butyne decomposed even at –20 °C after several days. These factors lead to a decrease in yield when using iodo derivatives as a starting material.

[21] After allenylations, milligram quantities of the corresponding alkyne iodides were isolated, in accordance with ref.[12b]

[22] In accordance with the observation of Lee: K. Lee, P. H. Lee, *Chem. Eur. J.* **2007**, *13*, 8877–8883.

[23] In the case of nBu$_4$NI, the corresponding propargyl iodide was isolated.

[24] a) E. Klaps, W. Schmid, *J. Org. Chem.* **1999**, *64*, 7537–7546; b) S. Araki, A. Imai, K. Shimizu, M. Yamada, A. Mori, Y. Butsugan, *J. Org. Chem.* **1995**, *60*, 1841–1847; c) S. Araki, F. Shiraki, T. Tanaka, H. Nakano, K. Subburaj, T. Hirahita, H. Yamamura, M. Kawai, *Chem. Eur. J.* **2001**, *7*, 2748–2790; d) L. A. Paquette, R. R. Rothhaar, *J. Org. Chem.* **1999**, *64*, 217–224.

[25] Synthesis of **2**: T. Nishiyama, T. Esumi, Y. Iwabuchi, H. Irie, S. Hatakeyama, *Tetrahedron Lett.* **1998**, *39*, 43–46. Synthesis of **4**: G. B. Jones, C. J. Moody, A. Padwa, J. M. Kassir, *J. Chem. Soc. Perkin Trans. 1* **1991**, 1721–1727. Synthesis of **5**: W. J. Bailey, E. Fujiwara, *J. Am. Chem. Soc.* **1955**, *77*, 165–166. Synthesis of **6**–**8** and **10**: see the Supporting Information. Compound **9** was purchased from Sigma–Aldrich.

[26] Diastereoselectivities were determined by ^{1}H NMR spectroscopy. a) M. T. Reetz, H. Haning, *J. Organomet. Chem.* **1997**, *541*, 117–120; b) L. A. Paquette, T. M. Mitzel, M. B. Isaac, C. F. Castro, W. W. Schomer, *J. Org. Chem.* **1997**, *62*, 4293–4301; c) P. Garner, J. M. Park, *J. Org. Chem.* **1987**, *52*, 2361–2364.

[27] In accordance with Li et al.: a) X.-H. Yi, Y. Meng, C.-J. Li, *Chem. Commun.* **1998**, 449–450; b) X.-H. Yi, Y. Meng, X.-G. Hua, C.-J. Li, *J. Org. Chem.* **1998**, *63*, 7472–7480.

[28] For the isolated side products see the Supporting Information: 5-[(benzyloxy)methyl]hepta-5,6-dien-1,4-diol (**30a**); 8-(benzyloxy)oct-6-yne-1,4-diol (**30b**); 1-*O*-benzyl-2,3-butadien-1-ol (**31a**); 1-*O*-benzylbut-2-yn-1-ol (**31b**).

[29] Previous synthesis of D-erythro-2-pentulose (**25**): see ref.[5a,5c,16b]; T. Vuorinen, A. S. Serianni, *Carbohydr. Res.* **1990**, *207*, 185–210.

[30] Previous synthesis of 1-deoxy-D-erythro-2-pentulose (**29**): a) J.-C. Fischer, D. Horton, W. Weckerle, *Can. J. Chem.* **1977**, *55*, 4078–4089; b) D. J. Hotchkiss, S. F. Jenkinson, R. Storer, T. Heinz, G. W. J. Fleet, *Tetrahedron Lett.* **2006**, *47*, 315–318; c) I. I. Cubero, M. T. P. Lopez-Espinosa, *Carbohydr. Res.* **1986**, *154*, 71–80; d) A. L. Concia, C. Lozano, J. A. Castillo, T. Parella, J. Joglar, P. Clapés, *Chem. Eur. J.* **2009**, *15*, 3808–3816; e) S. David, B. Estramareix, J.-C. Fischer, M. Thérisod, *J. Chem. Soc. Perkin Trans. 1* **1982**, 2131–2137.

[31] NMR spectroscopic study of 1-deoxy-D-erythro-2-pentulose (**29**): S. Köpper, S. Freimund, *Helv. Chim. Acta* **2003**, *86*, 827–843.

[32] E. Kim, D. M. Gordon, W. Schmid, G. M. Whitesides, *J. Org. Chem.* **1993**, *58*, 5500–5507.

[33] B. Alcaide, P. Almendros, T. Martínez del Campo, *Angew. Chem. Int. Ed.* **2006**, *45*, 4501–4504.

Received: October 22, 2010
Published Online: January 11, 2011

