A Convenient Approach to C_2-Chiral 1,1,4,4-Tetrasubstituted Butanetetraols: Direct Alkylation or Arylation of Enantiomerically Pure Diethyl Tartrates

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C_2-Chiral 1,1,4,4-tetraaryl- or 1,1,4,4-tetraalkyl-substituted butanetetraols have been conveniently synthesized *via* arylation or alkylation of unprotected diethyl (2*R*,3*R*)- and (2*S*,3*S*)-tartrates with *Grignard* reagent. The chiral 1,1,4,4-tetrasubstituted butanetetraols were characterized by IR, ^{1}H- and ^{13}C-NMR, as well as LC/MS.

1. Introduction. – Since *Frankland* and *Twiss* synthesized the first chiral 1,1,4,4-tetraphenylbutanetetraol derivative in 1904 [1], several hundred different analogs have already been described, and some of them have been successfully used as chiral ligand and auxiliaries in asymmetric synthesis[1]) and as chiral host in supramolecular chemistry [3]. However, it is really strange that the enantiomerically pure 1,1,4,4-tetrasubstituted butanetetraols as parent compound, except (2*R*,3*R*)-1,1,4,4-tetraphenylbutanetetraol [4], have been seldom reported to date. To the best of our knowledge, the known chiral 1,1,4,4-tetrasubstituted butanetetraol derivatives were prepared through alkylation or arylation of enantiomerically pure dialkyl tartrates 2,3-protected by an aldehyde or ketone with *Grignard* reagent; however, the deprotection of them to 1,1,4,4-tetrasubstituted butanetetraols or 2,3-diols turned out to be quite difficult, and more expensive reagents and rigorous conditions were required [5]. Recently, in the course of investigations on the chemistry of chiral 1,1,4,4-tetraphenylbutanetetraol, we observed that, under appropriate conditions, the threitol-derived compound could conveniently undergo highly regioselective 1,3- [6], 1,4- [7], or 2,3-cyclocondensation [8] and functional group transformation to furnish sterically hindered P-, S-, or B-functionalized diol compounds, which are considered as potential chiral catalysts for asymmetric synthesis and chiral hosts in supramolecular chemistry[2]). To study the

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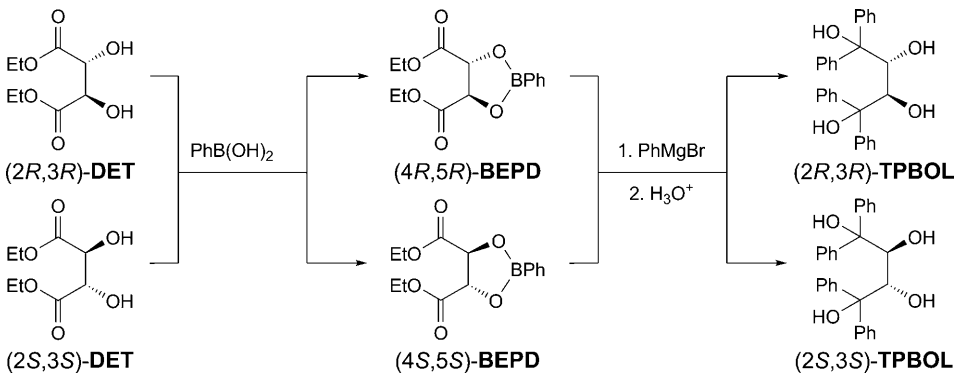
[1]) For recent reviews on tartaric acid derivatives and their application in asymmetric synthesis, see [2a–c]; for reviews on application of tartaric acid derivatives TADDOLs, see [2d][2e].

[2]) Our investigation has indicated that chiral (2*R*,3*R*)- and (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraols were readily available chiral starting materials, and they could be conveniently transformed into a variety of useful chiral ligands or auxiliaries for asymmetric synthesis *via* selective functional group transformation. For instance, (2*R*,3*R*)-1,1,4,4-tetraphenylbutanetetraol could be transformed into (2*R*,3*R*)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,2-diol *via* selective 2,3-bismethylation, (2*R*,3*R*)-1,1,4,4-tetraphenyl-1,4-dihydroxybutyl-2,3-diyl sulfite *via* selective 2,3-cyclosulfitation, and multi-functional chiral spiroboric esters, C_2-chiral spiroboric acid, or its salt *via* selective 2,3-cycloboration, *etc.*

chemistry of 1,1,4,4-tetrasubstituted butanetetraols and on search for highly effective chiral inducing agent, we explored some routes to C_2-chiral 1,1,4,4-tetrasubstituted butanetetraols. Here, we describe convenient preparations and properties for some representative enantiomerically pure 1,1,4,4-tetraaryl- or 1,1,4,4-tetraalkyl-substituted butanetetraols.

2. Results and Discussion. – 2.1. *Preparation of 1,1,4,4-Tetrasubstituted Butanetetraols.* Preparation of chiral 1,1,4,4-tetraphenylbutanetetraol was studied as a model. Considering that formation and cleavage of a B–O bond are easy, and boron derivatives are extensively used as protecting group of OH groups [9], alkylation and arylation of B-protected enantiomerically pure diethyl tartrates were tested. Phenylboronic acid ($PhB(OH)_2$)-protected diethyl tartrate was allowed to react with an excess of PhMgBr in THF, followed by hydrolysis under strong acidic condition in an ice-water bath to provide enantiomerically pure 1,1,4,4-tetraphenylbutanetetraol in good yield. For instance, diethyl (2*R*,3*R*)-tartrate reacted with $PhB(OH)_2$ in toluene under reflux to form a homogeneous solution of (4*R*,5*R*)-4,5-bis(ethoxycarbonyl)-2-phenyl-1,3,2-dioxaborolane (**BEPD**) after complete removal of H_2O. The solution was evaporated under reduced pressure to afford a viscous residue. The residue was dissolved in anhydrous THF, and then added dropwise under violent stirring to a freshly prepared PhMgBr/THF solution in a 1:5 molar ratio. The resultant mixture was stirred for 1 h at ambient temperature, refluxed for additional 1.5 h, then cooled with ice-water bath, and the reaction was finally quenched with aqueous HF or HCl to yield (2*R*,3*R*)-1,1,4,4-tetraphenylbutanetetraol from the organic phase (*Scheme 1*).

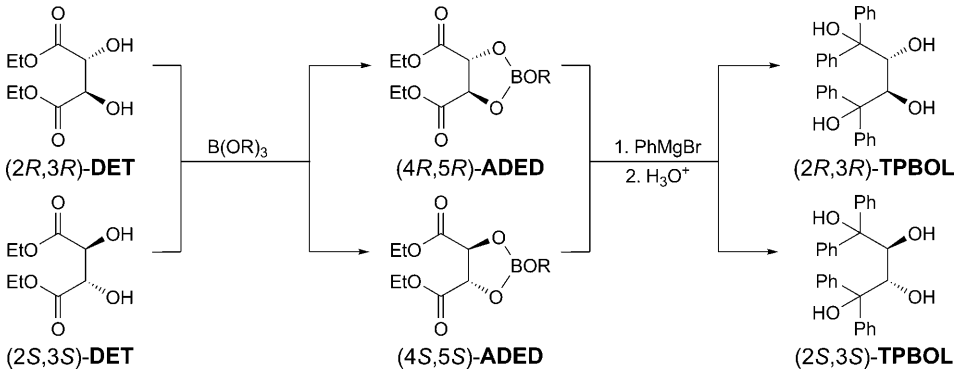
Scheme 1. *Preparation of Enantiomerically Pure 1,1,4,4-Tetraphenylbutanetetraols* via *Phenylation of Phenylboronic Acid-Protected Diethyl Tartrates with* Grignard *Reagent*



Taking into account that boronic acids are generally prepared through alkylation of trialkyl borate [10], the replacement of $PhB(OH)_2$ by trialkyl borate was considered. Diethyl (2*R*,3*R*)- or (2*S*,3*S*)-tartrate was allowed to react with trialkyl borate ($B(OR)_3$) by heating under solvent-free condition. After the resulting alkanol was distilled off under reduced pressure, a transparent viscous liquid of (4*R*,5*R*)- or (4*S*,5*S*)-2-alkoxy-4,5-bis(ethoxycarbonyl-1,3,2-dioxoborolane (**ADED**) was obtained. The viscous liquid was dissolved in anhydrous THF, and then reacted with freshly prepared PhMgBr in a

1:6 molar ratio. Acid hydrolysis as above gave (2*R*,3*R*)- or (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraol again in good yield (*Scheme 2*).

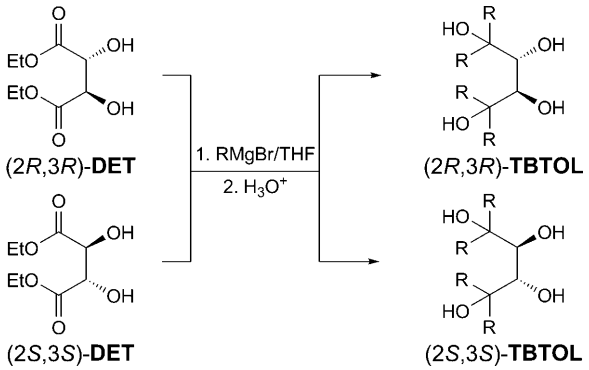
Scheme 2. *Preparation of Optically Pure 1,1,4,4-Tetraphenylbutanetetraols* via *Phenylation of Boric Ester-Protected Diethyl Tartrates with PhMgBr*



For a further simplification of the procedure, direct phenylation of the unprotected dialkyl tartrates was tested with the result that the reaction of diethyl (2*R*,3*R*)-tartrate with 5–6 equiv. of PhMgBr under conventional *Grignard* conditions also gave the desired products in moderate yield.

The above reactions were successfully applied to the preparation of other enantiomerically pure 1,1,4,4-tetrasubstituted butanetetraols having a C_2-axis of symmetry (*Scheme 3*). Some representative (2*R*,3*R*)- and (2*S*,3*S*)-1,1,4,4-tetraaryl- and 1,1,4,4-tetraalkylbutanetetraols prepared according to *Scheme 3* are listed in the *Table*.

Scheme 3. *Preparation of Optically Pure 1,1,4,4-Tetrasubstituted Butanetetraols* via *Direct Alkylation or Arylation of Diethyl Tartrates with RMgBr*



2.2. *Properties of 1,1,4,4-Tetrasubstituted Butanetetraols.* The chiral butanetetraols were characterized by IR, ^{1}H- and ^{13}C-NMR, and LC/MS. They are colorless solids, and the tetraarylbutanetetraols possess much higher melting points and specific rotations as

Table. *Preparation and Properties of C_2-Chiral 1,1,4,4-Tetrasubstituted Butanetetraols*[a])

	Diethyl tartrate	*Grignard* reagent	Butanetetraol[b]), R	M.p. [°][c]) $[\alpha]_D$[d]) ($CHCl_3$)	δ(H) [ppm][e])	
					C–H	OH
1	(2*S*,3*S*)	PhMgBr	Ph	149–150 – 156.6 ($c = 1.1$)	4.42	4.63/3.69
2	(2*R*,3*R*)	PhMgBr	Ph	150–151 + 154.0 ($c = 1.2$)	4.41	4.65/3.77
3	(2*R*,3*R*)	3-Me–C_6H_4MgBr	3-Me–C_6H_4	239–241 + 374 ($c = 1$)	4.48	4.56/3.69
4	(2*R*,3*R*)	2-Me–C_6H_4MgBr	2-Me–C_6H_4	232–235 + 362 ($c = 1$)	4.24	4.48/4.41
5	(2*R*,3*R*)	(Naphthalen-1-yl)MgBr	Naphthalen-1-yl	273–275 + 360 ($c = 1$)	4.61	5.02/4.86
6	(2*R*,3*R*)	(Hexyl)MgBr	Hexyl	71–72 + 4.3 ($c = 1$)	3.65	4.03/2.96
7	(2*R*,3*R*)	BuMgBr	Bu	80–82 + 6.2 ($c = 1$)	3.65	4.07/3.00

[a]) All products were obtained through direct alkylation of dialkyl (2*R*,3*R*)- and (2*S*,3*S*)-tartrates with 7 equiv. of RMgBr. [b]) For the formulae of the butanetetraols, see *Scheme 3*. [c]) Uncorrected. [d]) 10–30°. [e]) Chemical shifts ($CDCl_3$) of the framework and OH H-atoms of the tetraols; for compound **4**, in (D_6)DMSO, the chemical shifts of H–C(2,3) at 4.16 ppm, and those of the four OH groups are at 6.27 and 5.27 ppm, respectively.

compared with the tetraalkylbutanetetraols (*Table*). The ^{1}H-NMR spectra showed three sets of resonances in an intensity ratio of 1:1:1 in the region of *ca.* 5.1 to 2.9 ppm, and two of the signals disappeared after the addition of D_2O. Obviously, these molecules possess two equivalent framework CH groups and two sets of nonequivalent OH groups. It was further noticed that the resonances of the tetraarylbutanetetraols appeared at 4.41 ± 0.20 for H–C(2,3) and at 4.75 ± 0.30 and 4.28 ± 0.59 ppm for the OH groups, whereas those of the tetraalkylbutanetetraols showed up at 3.65, and 4.05 ± 0.02, and 2.98 ± 0.02 ppm, respectively, almost regardless of the length of the alkyl chain. The signals of 1,1,4,4-tetranaphthalen-1-ylbutanetetraols were observed at lowest field (4.61, 5.02, and 4.86 ppm). These observations reveal that the introduction of aryl groups at C(1) and C(4) not only influences the chemical-shift of HO–C(1,4), but also induces a downfield shift of H–C(2,3) and HO–C(2,3). It was also observed that, in most cases, the resonance of the framework H–C(2,3) exhibited a *doublet*, which was changed to a *singlet* after addition of D_2O, implying vicinal CH,OH coupling. As far as the resonances of the OH groups are concerned, there are two sets of chemical shifts, for all tetrasubstituted butanetetraols, and the chemical shift difference ($\Delta\delta$) between them is 1.0 ± 0.1 ppm, which is reduced in the case of **4** (0.07 ppm) and **5** (0.16 ppm). The downfield OH signal (*s*) has to be attributed to HO–C(1,4), while the upfield OH signal (*s* or *d*) has to be assigned to OH–C(2,3). Since intramolecular H-bonding interaction between HO–C(1) and HO–C(3) in a cycloborate derivative of 1,1,4,4-tetraphenylbutanetetraol has been established by a single-crystal X-ray diffraction analysis [11], it is assumed that the OH groups of the butanetetraols are in similar H-bonding environment, and it may be estimated, based on the above discussion, that the H-atoms of HO–C(1,4) are the donators, while the O-atoms of HO–C(2,3) are the acceptors (*Fig.*). The ^{13}C-NMR spectra exhibited two peaks at 81 ± 3 and 71 ± 1.5 ppm, which corresponded to the quaternary C-atoms C(1) and C(4), and the tertiary C-atoms C(2) and C(3), respectively, revealing that only two types of framework C-atoms are involved in the butanetetraol molecules in agreement with the average C_2-symmetry of the starting material. The above data indicate that the

electronic properties of the substituents at C(1) and C(4) do not markedly influence the chemical shifts for the framework C-atoms. Compared with unsubstituted butanetetraol (at *ca.* 73 ppm and 64 ppm [12]), the resonance of C(2) and C(3) merely shifts slightly upfield, while for C(1) and C(4), the change from primary to quaternary C-atom results in downfield shifts by 14 – 20 ppm.

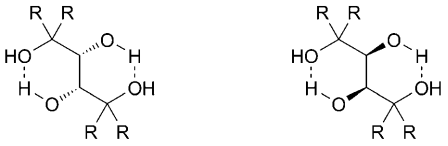


Figure. *Proposed intramolecular H-bonding in 1,1,4,4-tetrasubstituted butanetetraols*

3. Conclusions. – In summary, convenient accesses to 1,1,4,4-tetrasubstituted (2*R*,3*R*)- and (2*S*,3*S*)-butanetetraols have been developed. Boron-protected and unprotected enantiomerically pure diethyl (2*R*,3*R*)- and (2*S*,3*S*)-tartrates reacted with excess *Grignard* reagent under conventional *Grignard* reaction condition to furnish C_2-chiral 1,1,4,4-tetrasubstituted butanetetraols in moderate yield, which are potential, readily available chiral starting materials for the preparation of a variety of chiral inductors.

Experimental Part

General. Commercially available starting materials and solvents were used without further purification if not specified. M.p.: *VEB Wägetechnik Rapido PHMK 05* instrument; uncorrected. Optical rotations: in $CHCl_3$, on a *Perkin-Elmer 341 Mc* polarimeter. IR Spectra (KBr): *Testscan Shimadzu FTIR 8000*, and selected characteristic absorptions reported in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Varian Mercury VX 300* NMR spectrometer in $CDCl_3$; chemical shifts relative to TMS (internal standard). All known products were confirmed by comparison of their data with those of authentic samples.

*Preparation of (2*R*,3*R*)- and (2*S*,3*S*)-1,1,4,4-Tetrasubstituted Butanetetraols. Preparation of Chiral 1,1,4,4-Tetraphenylbutanetetraol* via *the Phenylation of B-Protected Diethyl Tartrates.* Diethyl (2*R*,3*R*)- or (2*S*,3*S*)-tartrate was allowed to react with $PhB(OH)_2$ or $B(OR)_3$ in toluene under reflux, until a homogeneous soln. was formed. The soln. was evaporated under reduced pressure, and the residue was taken up in anh. THF and added dropwise under violent stirring to a freshly prepared *Grignard* reagent (PhMgBr/boronate 1:4 to 6). After complete addition, the mixture was stirred for an additional hour at r.t., and then refluxed for 1.5 h, cooled to r.t., and further cooled to 0° (ice-water bath). Addition of HF or 6M HCl under stirring resulted in two liquid layers. The org. phase was separated, and the H_2O layer was extracted with Et_2O. The combined org. phases were dried (Na_2SO_4), concentrated, and then separated by column chromatography (CC) to furnish (2*R*,3*R*)- or (2*S*,3*S*)-1,1,4,4-tetraphenylbutanetetraol in *ca.* 50% yield.

Representative Procedure for the Synthesis of Chiral 1,1,4,4-Tetrasubstituted Butanetetraols by Direct Alkylation of Enantiomerically Pure Diethyl Tartrates. (Naphthalen-1-yl)magnesium bromide, prepared from Mg turnings (6.65 g, 277 mmol) and 1-bromonaphthalene (35 ml, *ca.* 251 mmol) in THF (100 ml), was cooled to 0°, followed by dropwise addition of the soln. of diethyl (2*R*,3*R*)-tartrate (6.18 g, 30 mmol) in 10 ml anh. THF with vigorous stirring. After complete addition, the soln. was warmed to r.t. and stirred for 1 additional h. Then, the soln. was heated and refluxed for another 1.5 h, cooled to r.t., followed by addition of 200 ml of a cooled sat. aq. NH_4Cl soln. under stirring. The org. layer was separated, and the

aq. layer was extracted with Et_2O (3×15 ml). The org. phases were combined and dried (Na_2SO_4). A yellow, viscous residue was obtained after concentration. The residue was purified through CC on silica gel (petroleum ether/AcOEt/CH_2Cl_2 6:1:0.4) to give white crystals of *(2R3R)-1,1,4,4-tetra(naphthalen-1-yl)butane-1,2,3,4-tetrol* (**5**; 9.8 g, 52%; based on diethyl (2*R*,3*R*)-tartrate). M.p. 273–275°. $[\alpha]_D^{25} = +360$ ($c = 1$, $CHCl_3$). IR: 3410v*s* (br., OH), 3045*m* (Ar–H), 2926*m* (C–H), 1646*m*, 1635*m*, 1509*m* (Ar backbone), 1385*s* (C–H), 1114*s* (C–O), 802*m*, 775*s* (Ar–H). ^{1}H-NMR: 8.73–8.72 (*m*, 2 arom. H); 8.46–8.43 (*m*, 2 arom. H); 7.83 (*d*, $J = 7.2$, 4 arom. H); 7.71–7.56 (*m*, 8 arom. H); 7.43–7.38 (*m*, 2 arom. H); 7.28 (*s*, 2 arom. H); 7.23–7.20 (*m*, 2 arom. H); 7.18–7.07 (*m*, 2 arom. H); 6.86 (*s*, 2 arom. H); 6.64–6.62 (*m*, 2 arom. H); 6.03 (*d*, $J = 3$, 2 arom. H); 5.02 (*s*, 2 OH); 4.86 (*s*, 2 OH); 4.61 (*s*, 2 H–C). ^{13}C-NMR ($CDCl_3$, 75 MHz): 135.1; 129.6; 129.4; 128.8; 128.5; 126.9; 125.4; 124.9; 124.4; 83.5; 72.0. LC/MS: 625 (24, $[M-1]^+$), 431 (26, $[M - Ar - 4\ OH]^+$).

By similar procedures, other 1,1,4,4-tetrasubstituted butanetetraols were obtained.

(2S,3S)-1,1,4,4-Tetraphenylbutane-1,2,3,4-tetraol (**1**). Yield 48%. M.p. 149–150°. $[\alpha]_D^{25} = -156.6$ ($c = 1.1$, $CHCl_3$). IR: 3437, 3058, 2916, 1598, 1492, 1447, 1062, 698. ^{1}H-NMR: 7.37–7.13 (*m*, 20 arom. H); 4.63 (*d*, $J = 4.8$, 2 OH, disappeared after adding D_2O); 4.42 (*d*, $J = 4.5$, 2 H–C); 3.69 (*d*, $J = 4.8$, 2 OH, disappeared after adding D_2O). ^{13}C-NMR: 143.8; 142.7; 134.6; 131.5; 129.3; 128.3; 128.2; 127.9; 127.5; 126.7; 125.5; 81.1; 69.7.

(2R,3R)-1,1,4,4-Tetraphenylbutane-1,2,3,4-tetraol (**2**). Yield 43%. M.p. 150–151° ([4]: 148–151°). $[\alpha]_D^{25} = +154$ ($c = 1.2$, $CHCl_3$; [4]: $[\alpha]_D = +164$ ($c = 0.51$, $CHCl_3$)). IR: 3436, 3058, 2916, 1598, 1492, 1447, 1063, 698. ^{1}H-NMR: 7.37–7.13 (*m*, 20 arom. H); 4.65 (*d*, $J = 7.2$, 2 OH, disappeared after adding D_2O); 4.41 (*d*, $J = 4.7$, 2 H–C); 3.77 (*d*, $J = 5.3$, 2 OH, disappeared after adding D_2O). ^{13}C-NMR ($CDCl_3$, 75 MHz): 143.8; 142.7; 134.6; 131.5; 129.3; 128.3; 128.2; 127.9; 127.5; 126.7; 125.5; 81.3, 69.7.

(2R,3R)-1,1,4,4-Tetrakis(3-methylphenyl)butane-1,2,3,4-tetraol (**3**). Yield 54%. M.p. 239–241°. $[\alpha]_D^{25} = +374$ ($c = 1$, $CHCl_3$). ^{1}H-NMR: 7.26–7.10 (*m*, 12 arom. H); 7.05–7.00 (*m*, 4 arom. H); 4.56 (*s*, 2 OH, disappeared after adding D_2O); 4.48 (*d*, $J = 4.5$, 2 H–C); 3.69 (*d*, $J = 5.1$, 2 OH, disappeared after adding D_2O); 2.35 (*s*, 2 Me); 2.23 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): 141.6; 141.4; 136.9; 129.4; 129.2; 126.0; 125.1; 81.58; 72.38; 21.31; 21.30. LC/MS: 505 (24, $[M + Na]^+$).

(2R,3R)-1,1,4,4-Tetrakis(2-methylphenyl)butane-1,2,3,4-tetraol (**4**). Yield 54%. M.p. 232–234°. $[\alpha]_D^{25} = +362$ ($c = 1$, $CHCl_3$). ^{1}H-NMR: 7.40–6.90 (*m*, 12 arom. H); 4.48 (*s*, 2 OH, disappeared after adding D_2O); 4.24 (*d*, $J = 4.5$, 2 H–C); 4.41 (*d*, $J = 5.1$, 2 OH, disappeared after adding D_2O); 1.95 (*s*, 4 Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): 140.4; 138.8; 132.9; 132.5; 129.1; 127.8; 126.9; 126.0; 124.8; 82.95; 70.34; 21.47. LC/MS: 481 (52, $[M-1]^+$).

(8R,9R)-7,10-Dihexylhexadecane-7,8,9,10-tetraol (**6**). Yield 43%. M.p. 71–72°. $[\alpha]_D^{25} = +4.3$ ($c = 1$, $CHCl_3$). IR: 3410, 2953, 2922, 2859, 1462. ^{1}H-NMR: 4.03 (*d*, $J = 3.6$, 2 OH, disappeared after adding D_2O); 3.65 (*d*, $J = 2.7$, 2 H–C); 2.96 (*s*, 2 OH, disappeared after adding D_2O); 1.57–0.89 (*m*, 52 H–C). ^{13}C-NMR ($CDCl_3$, 75 MHz): 78.2; 72.2; 35.0; 34.5; 32.0; 31.9; 30.1; 30.0; 23.5; 23.4; 22.9; 22.8; 14.2. LC/MS: 457 (52, $[M-1]^+$).

(6R,7R)-5,8-Dibutyldodecane-5,6,7,8-tetraol (**7**). Yield 41%. M.p. 80–82°. $[\alpha]_D^{25} = +6.2$ ($c = 1$, $CHCl_3$). IR: 3412, 2954, 2928, 2860, 2872, 1466. ^{1}H-NMR: 4.07 (*s*, 2 OH, disappeared after adding D_2O); 3.65 (*s*, 2 H–C); 3.00 (*d*, 2 H, $J = 5.1$, OH, disappeared after adding D_2O); 1.69–0.92 (*m*, 36 H–C). ^{13}C-NMR ($CDCl_3$, 75 MHz): 78.1; 72.2; 34.7; 34.2; 25.8; 25.7; 23.5; 23.4; 14.3. LC/MS: 345 (100, $[M-1]^+$).

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REFERENCES

[1] P. F. Frankland, D. F. Twiss, *J. Chem. Soc., Trans.* **1904**, *85*, 1666.

[2] a) L. Synoradzki, P. Ruskowski, U. Bernaś, *Org. Prep. Proced. Int.* **2005**, *37*, 37; b) A. K. Ghosh, E. S. Koltun, G. Bilcer, *Synthesis* **2001**, 1281; c) K. Ilmarinen, K. Kriis, A. Paju, T. Pehk, M. Lopp, *Proc. Est. Acad. Sci., Chem.* **2001**, *50*, 147; d) D. Seebach, A. K. Beck, A. Heckel, *Angew. Chem., Int. Ed.* **2001**, *40*, 92–138; e) A. K. Beck, R. Dahinden, F. N. M. Kuhnle, *ACS Symp. Ser.* **1996**, *641*, 52.

[3] K. Tanaka, H. Takenaka, M. R. Caira, *Tetrahedron: Asymmetry* **2006**, *17*, 2216; K. Tanaka, D. Kuchiki, M. R. Caira, *Tetrahedron: Asymmetry* **2006**, *17*, 1678; S. Legrand, H. Luukinen, R. Isaksson, I. Kilpeläinen, M. Lindström, I. A. Nicholls, C. R. Unelius, *Tetrahedron: Asymmetry* **2005**, *16*, 635; F. Toda, H. Miyamoto, T. Tamashima, M. Kondo, Y. Ohashi, *J. Org. Chem*. **1999**, *64*, 2690; D. Hashizume, H. Uekusa, Y. Ohashi, R. Matsugawa, H. Miyamoto, F. Toda, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 985; F. Toda, K. Tanaka, L. Nassimbeni, M. Niven, *Chem. Lett.* **1988**, *17*, 1371; F. Toda, K. Tanaka, *J. Org. Chem*. **1988**, *53*, 3607.

[4] F. Toda, K. Tanaka, *Tetrahedron Lett.* **1988**, *29*, 551.

[5] J. E. A. Luithle, J. Pietruszka, *J. Org. Chem.* **1999**, *64*, 8287; K. Nakayama, J. D. Rainier, *Tetrahedron* **1990**, *46*, 4165.

[6] Z. Shan, X. Hu, Y. Zhou, X. Peng, J. Yi, *Tetrahedron: Asymmetry,* **2009**, *20*, 1445.

[7] X. Hu, Z. Shan, X. Peng, Z. Li, *Tetrahedron: Asymmetry* **2009**, *20*, 2474.

[8] Z. X. Shan, S. J. Song, X. Y. Hu, B. B. Wu, G. X. Xia, 'The 6th National Symposium on Organic Chemistry of Chinese Chemical Society', 2009.

[9] G. A. Molander, N. Ellis, *Acc. Chem. Res.* **2007**, *40*, 275; P. J. Duggan, E. M. Tyndall, *J. Chem. Soc., Perkin Trans. 1* **2002**, 1325; D. A. Evans, F. Glorius, J. D. Burch, *Org. Lett.* **2005**, *7*, 3331; H. R. Bjørsvik, H. Priebe, J. Cervenka, A. W. Aabye, T. Gulbrandsen, A. C. Bryde, *Org. Proc. Res. Dev.* **2001**, *5*, 472; W. Bauer, J. Pless, 'Pept.: Chem., Struct. Biol., Proc. Am. Pept. Symp.', 4th Edn. Eds. R. Walter, J. Meienhofer, 1975, pp. 341 – 345.

[10] D. G. Hall, 'Boronic Acids', Wiley-VCH, Weinheim, 2005, pp. 1 – 99; M. Murata, *Fain Kemikaru* **2006**, *35*, 25 (*Chem. Abstr.* **2006**, *146*, 100738); Y. Q. Li, Y. C. Peng, *Huaxue Shiji* **2006**, *28*, 149 (*Chem. Abstr.* **2006**, *145*, 505492); N. Miyaura, *Farumashia* **2004**, *40*, 1103 (*Chem. Abstr.* **2004**, *142*, 155990); R. Zenk, S. Partzsch, *Chim. Oggi* **2003**, *21*, 70 (*Chem. Abstr.* **2003**, *140*, 303709); H. Carlsohn, M. Hartmann, *Acta Polym.* **1979**, *30*, 420; B. Serafinowa, *Wiadomosci Chem.* **1968**, *22*, 819 (*Chem. Abstr.* **1969**, *70*, 106584).

[11] Y. Zhou, Z. Shan, *Tetrahedron Lett.* **2007**, *48*, 3531.

[12] R. N. Monrad, R. Madsen, *J. Org. Chem.* **2007**, *72*, 9782.

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