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Asymmetric Dihydroxylations of 1-Substituted (*E*)- and (*Z*)-3-Methylpent-2-en-4-ynes: Full Compliance with the Sharpless Mnemonic Re-established and Embellished

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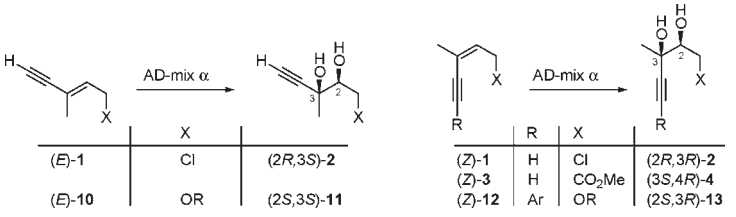
ABSTRACT



Asymmetric dihydroxylations ("ADs") of the pentenynyl chlorides (*E*)- and (*Z*)-1 or the pentenyne-based ester (*Z*)-3 in the presence of $(DHQ)_2$-containing ligands delivered diol stereoisomers (2*R*,3*S*)-2, (2*R*,3*R*)-2, and (3*S*,4*R*)-4, respectively. The ADs of pentenynyl ethers (*E*)-10 and (*Z*)-12, respectively, have the same stereochemical preference under analogous conditions; these reattributions correct previous reports of the contrary. The Sharpless mnemonic rationalizes all these results implying that each substrate prefers a Sharpless/Norrby instead of a Chapleur orientation in the transition state.

Recently[1] we have shown that in the presence of Sharpless' ligands $(DHQ)_2PHAL$ (which is responsible for stereocontrol effected by AD-mix α[2]) or $(DHQ)_2AQN$[3] the 1-chlorinated 3-methylpent-2-en-4-ynes (*E*)- and (*Z*)-**1** are dihydroxylated asymmetrically.[4] This furnished chlorodiols (2*R*,3*S*)- and (2*R*,3*R*)-**2**, respectively, in yields of up to 73% (Scheme 1). Enantioselectivities reached 85% *ee* with (*E*)-**1** as the substrate and 91% *ee* starting from (*Z*)-**1**. The configurational proof in the (*E*)-series was based on an X-ray structural analysis and the proof in the (*Z*)-series on a correlation with a compound derived from the (*E*)-series.

Another 1-substituted 3-methylpent-2-en-4-yne, namely ester (*Z*)-**3**, reacted with the same facial selectivity with Sharpless' AD-mix α as chloride (*Z*)-**1**, proceding via dihydroxyester (3*S*,4*R*)-**4** directly[5] to the hydroxylactone (4*S*,5*R*)-**5**[6] (Scheme 2). The correct configuration of the latter was not recognized correctly[7] before we found that ester (*Z*)-**6** and AD-mix α gave the *identically* configured lactone (4*S*,5*R*)-**8** via dihydroxyester (3*S*,4*R*)-**7**.[8] This was shown by an X-ray analysis of the derived bromobenzoate

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(1) Burghart-Stoll, H.; Kapferer, T.; Brückner, R. *Org. Lett.* (DOI: 10.1021/OL103061g).
(2) (a) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768–2771 (in the presence of $MeSO_2NH_2$). (b) Footnote 6 in Jeong, K.-S.; Sjö, P.; Sharpless, K. B. *Tetrahedron Lett.* **1992**, *33*, 3833–3836 (in the absence of $MeSO_2NH_2$).
(3) (a) Becker, H.; Sharpless, K. B. *Angew. Chem.* **1996**, *108*, 447–449. (b) Becker, H.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 448–451.

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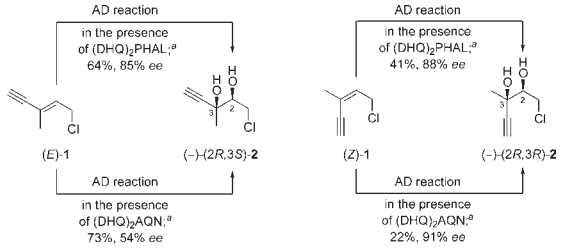
Scheme 1. AD Reactions of the Methylpentenyne-Based Chlorides (*E*)- and (*Z*)-**1**

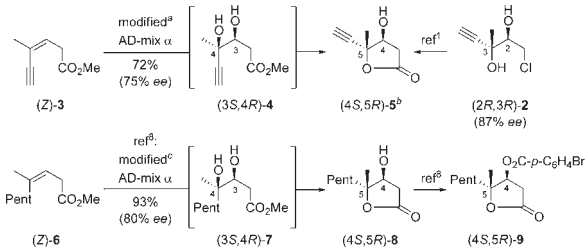


[a] $K_3Fe(CN)_6$ (3.0 equiv), $K_2OsO_2(OH)_4$ (1.0 mol %), dihydroquinidine-based ligand (2.0 mol %), buffer (3.0 equiv each of $NaHCO_3$ and K_2CO_3), and $MeSO_2NH_2$ (1.0 equiv).

(4*S*,5*R*)-**9**. A *proof* of the steric course of the AD reaction of ester (*Z*)-**3** was obtained by an independent synthesis[1] of the same lactone (4*S*,5*R*)-**5** from the chlorodiol (2*R*,3*R*)-**2**.

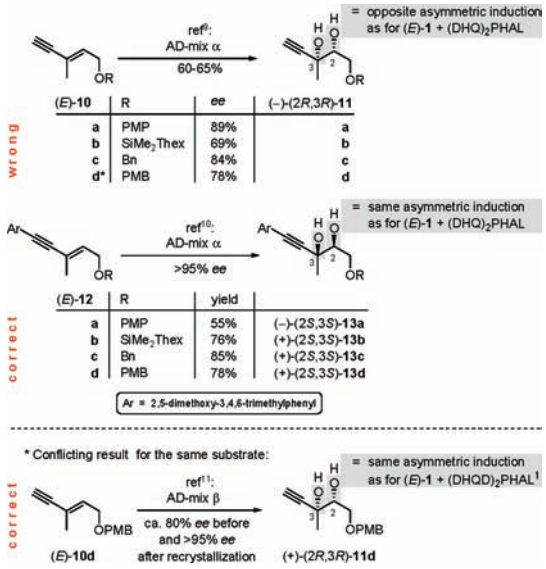
Disconcertingly, the stereoselectivity of our AD (*E*)-**1** + AD-mix α → (2*R*,3*S*)-**2** differed from the selectivities reported for ADs of certain ethers, which share an (*E*)-configured methylpentenyne with our substrate: AD-mix α was claimed to convert ethers (*E*)-**10a**−**d** into diols (2*R*,3*R*)-**11a**−**d** (Scheme 3, top).[9] Similarly, our ADs (*Z*)-**1** + AD-mix α → (2*R*,3*R*)-**2** and (*Z*)-**3** + AD-mix α → (3*S*,4*R*)-**4**/(4*S*,5*R*)-**5** had opposite stereoselectivities as the ADs of several ethers, which share a (*Z*)-configured methylpentenyne with our substrates: AD-mix α allegedly transforms ethers (*Z*)-**12a** and **b** into dihydroxyethers (2*R*,3*S*)-**13a** and **b**, respectively (Scheme 4, bottom).[10] Incidentally Nakatani et al. (Scheme 3, bottom) contradicted this (without recognizing it) when they dihydroxylated the PMB ether (*E*)-**10d** in the presence of AD-mix β and isolated diol

Scheme 2. AD Reactions of the Methylpentenyne-Based Ester (*Z*)-**3** and the Related Ester (*Z*)-**6**[8]



[a] $K_3Fe(CN)_6$ (3.0 equiv), $K_2OsO_2(OH)_4$ (2.0 mol %), $(DHQ)_2PHAL$ (10 mol %), K_2CO_3 (3.0 equiv), and $MeSO_2NH_2$ (1.0 equiv). [b] Prepared from (*Z*)-**3**: $[\alpha]_D^{20} = -4.9$ ($c = 0.83$ in $CHCl_3$); prepared from (2*R*,3*R*)-**2**: $[\alpha]_D^{20} = -5.6$ ($c = 0.5$ in $CHCl_3$). [c] $K_3Fe(CN)_6$ (3.0 equiv), $K_2OsO_2(OH)_4$ (0.8 mol %), $(DHQ)_2PHAL$ (1.6 mol %), K_2CO_3 (3.0 equiv), and $MeSO_2NH_2$ (1.0 equiv).

Scheme 3. AD Reactions of the Methylpentenyne-Based Ethers (*E*)-**10**[9] and (*E*)-**12**[10] from the Literature[11,12]



(2*R*,3*R*)-**11d**, which was dextrorotatory.[11] According to Tietze and Görlitzer the same diol (2*R*,3*R*)-**11d** stemmed from (*E*)-**10d** and AD-mix α but was levorotatory.[9]

Ancillary findings by Tietze and Görlitzer increased our worries. Ethers (*E*)-**12a**−**d** and AD-mix α reportedly gave the diols (2*S*,3*S*)-**13a**−**d** (Scheme 3, center);[10] this amounts to a *reversal* of the asymmetric induction in the ADs (*E*)-**10a**−**d** + AD-mix α → (2*R*,3*R*)-**11a**−**d**[9] (Scheme 3, top). Why an *sp*-bonded arene moiety in (*E*)-**12a**−**d** instead of an *sp*-bonded H-atom in (*E*)-**10a**−**d** should have such an

(4) (a) Lohray, B. B. *Tetrahedron: Asymmetry* **1992**, *3*, 1317–1349. (b) Johnson, R. A.; Sharpless, K. B. In *Asymmetric Catalysis in Organic Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp 227−272; (c) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–2547. (d) Poli, G.; Scolastico, C. *Methoden Org. Chem. (Houben-Weyl)*, 4th ed. −, Vol. E21e; Helmchen, G., Hoffmann, R. W., Mulzer, J., Schaumann, E., Eds.; Thieme: Stuttgart, 1995; pp 4547−4598. (e) Salvadori, P.; Pini, D.; Petri, A. *Synlett* **1999**, 1181–1190. (f) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 357−389. (g) Bolm, C.; Hildebrand, J. P.; Muñiz, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: Weinheim, 2000; pp 399−428. (h) Krief, A.; Colaux-Castillo, C. *Pure Appl. Chem.* **2002**, *74*, 107–113. (i) Kolb, H. C.; Sharpless, K. B. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 275−298. (j) Noe, M. C.; Letavic, M. A.; Snow, S. L.; McCombie, S. *Org. React.* **2005**, *66*, 109–625. (k) Zaitsev, A. B.; Adolfsson, H. *Synthesis* **2006**, 1725–1756.

(5) Method: (a) Harcken, C.; Brückner, R. *Angew. Chem.* **1997**, *109*, 2866–2868. Harcken, C.; Brückner, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 2750–2752. (b) Kapferer, T.; Brückner, R. *Eur. J. Org. Chem.* **2006**, 2119–2133.

(6) The enantiopurity of *this* specimen was determined by chiral HPLC after *tert*-butyldiphenylsilylation (see Supporting Informations).

(7) Böhnke, O. *Dissertation*, Universität Freiburg, 2002, pp 63, 124, 151.

(8) Kapferer, T.; Brückner, R.; Herzig, A.; König, W. A. *Chem.—Eur. J.* **2005**, *11*, 2154–2162.

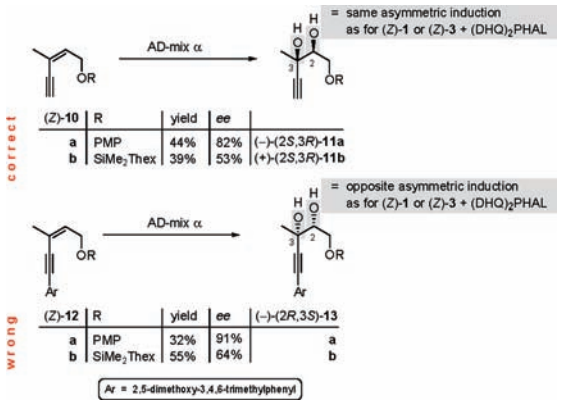
(9) Tietze, L. F.; Görlitzer, J. *Liebigs Ann. Recl.* **1997**, 2221–2225.

(10) Tietze, L. F.; Görlitzer, J. *Synthesis* **1997**, 877–885.

(11) (a) Nakatani, K.; Okamoto, A.; Saito, I. *Angew. Chem.* **1997**, *109*, 2881–2884. Nakatani, K.; Okamoto, A.; Saito, I. *Angew. Chem., Int. Ed.* **1997**, *36*, 2794–2797. (b) Nakatani, K.; Okamoto, A.; Matsuno, T.; Saito, I. *J. Am. Chem. Soc.* **1998**, *120*, 11219–11225.

(12) The AD reaction of the *para*-methoxybenzoate of the alcohol, which underlies the ethers (*E*)-**10a**−**d**, in the presence of AD-mix α gave a levorotatory triol with 86% *ee*; the "configuration of the major enantiomer was assigned tentatively by application of the Sharpless mnemonic" as (2*S*,3*S*), i.e. differently than Tietze's (2*R*,3*R*)-**10a**−**d**: Alvarez, S.; Alvarez, R.; de Lera, A. R. *Tetrahedron Asymmetry* **2004**, *15*, 839–846. Our results are analogous and therefore corroborate de Lera's conclusion.

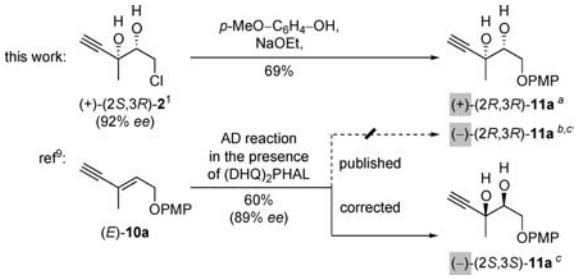
Scheme 4. AD Reactions of the Methylpentenyne-Based Ethers (*Z*)-**10**[9] and (*Z*)-**12**[10] from the Literature[14]



effect was not clear.[13] The same structural change seemed to swap the asymmetric inductions in the AD-mix α-mediated dihydroxylations of the C_{sp}-arylated ethers (*Z*)-**12a**,**b** [→ (2*R*,3*S*)-**13a** and **b**, respectively;[10] Scheme 4, bottom] compared to the C_{sp}-unsubstituted ethers (*Z*)-**10a**,**b** [→ (2*R*,3*S*)-**11a** and **b**, respectively;[9] Scheme 4, top].

The pivotal role of Sharpless ADs in organic synthesis[4] compelled us to check these matters by correlating selected Tietze/Görlitzer diols with ours. We showed both for ether (*E*)-**10a** and ether (*Z*)-**12a,b**—i.e., for representative

Scheme 5. AD Reactions Reassigned I: Proof That (*E*)-**10a** and AD-Mix α React Differently than Published



[a] $[\alpha]_D^{20} = +23.6$ ($c = 1.1$ in $CHCl_3$). [b] Compatibility of this sense of the specific rotation with the depicted configuration is excluded by our work. [c] $[\alpha]_D^{20} = -22.0$ ($c = 1.0$ in $CHCl_3$).

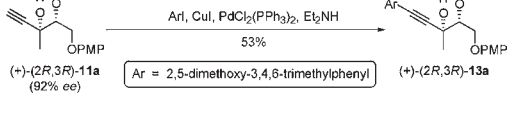
substrates—that the stereodescriptors of the resulting diols must be reversed (Schemes 5 and 6, respectively). Moreover we proved the correctness of the stereodescriptors of diol (2*S*,3*S*)-**13a**[15−18] obtained from ether (*E*)-**12a** and of diol (2*S*,3*R*)-**11a**[19,20] obtained from ether (*Z*)-**10a**.

Chlorodiol (2*S*,3*R*)-**2**[1] and sodium 4-methoxyphenoxide in ethanol[21] at reflux gave the PMP-containing diol (2*R*,3*R*)-**11a** (Scheme 5). It was dextrorotatory. Diol **11a** prepared from the PMP ether (*E*)-**10a** and AD-mix α was levorotatory[9] and therefore (2*S*,3*S*)-**11a**.[22] By analogy, diols (−)-**11b**−**c** of Scheme 3 should be (2*S*,3*S*)-configured, too.

(13) There are AD reactions, however, where remote anisyl groups modify the extent of enantiocontrol, albeit not its direction: (a) Corey, E. J.; Guzman-Perez, A.; Noe, M. C. *Tetrahedron Lett.* **1995**, *36*, 3481–3484. (b) Corey, E. J.; Guzman-Perez, A.; Noe, M. C. *J. Am. Chem. Soc.* **1995**, *117*, 10805–10816. (c) Corey, E. J.; Noe, M. C.; Guzman-Perez, A. *J. Am. Chem. Soc.* **1995**, *117*, 10817–10824. (d) Corey, E. J.; Noe, M. C.; Ting, A. Y. *Tetrahedron Lett.* **1996**, *37*, 1735–1738. (e) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 11038–11053.

(14) The AD reaction of the *para*-methoxybenzoate of the alcohol, which underlies the ethers (*Z*)-**10a**,**b**, with AD-mix α gave a levorotatory triol with 56% *ee*; the "absolute configuration of the major enantiomer was assigned tentatively by application of the Sharpless mnemonic" as (2*S*,3*R*), i.e. differently than Tietze's (2*R*,3*S*)-**12a**,**b**: Alvarez, S.; Alvarez, R.; de Lera, A. R. *Tetrahedron Asymmetry* **2004**, *15*, 839–846. Our results are analogous and therefore corroborate de Lera's conclusion.

(15) We proved the steric course of Tietze's and Görlitzer's transformation[9] (*E*)-**12a** + AD-mix α → (−)-(2*S*,3*S*)-**13a** (Scheme 3, center) by gaining the enantiomeric product (+)-(2*R*,3*R*)-**13a** by a Sonogashira coupling between diol (+)-(2*R*,3*R*)-**11a** (proof of the 3D structure of the latter: Scheme 5, top) and 1-iodo-2,5-dimethoxy-3,4,6-trimethylbenzene.[18] (2*S*,3*S*)-**13a** (>95% *ee*) exhibited $[\alpha]_D^{20} = -13.5$ ($c = 1$ in $CHCl_3$) whereas (2*R*,3*R*)-**13a** (92% *ee*) exhibited $[\alpha]_D^{20} = +11.4$ ($c = 0.3$ in $CHCl_3$); i.e., these compounds had inverse rotational powers.



(16) The steric course of the transformation (*E*)-**12b** + AD-mix α → (2*S*,3*S*)-**13b** (Scheme 3, center) was established unambiguously by acetonide formation, desilylation, condensation with (−)-camphanoyl chloride, and an X-ray structural analysis of the resulting ester.[10]

(17) Differently than stated[10] no proof was provided for the stereoselectivity of the transformation (*E*)-**12c** + AD-mix α → (2*S*,3*S*)-**13c** (Scheme 3, center): (2*S*,3*S*)-**13c** had been converted into what was drawn as the *S*-enantiomer of 6-(benzyloxy)-2,5,7,8-tetramethylchromane-2-carbaldehyde in seven steps,[10] but this assignment was not corroborated experimentally.[18]

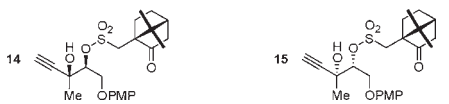
(18) (*S*)-6-(Benzyloxy)-2,5,7,8-tetramethylchromane-2-carbaldehyde is dextrorotatory (589 nm, $c = 5.2$ in $CHCl_3$) according to Cohen, N.; Lopresti, R. J.; Saucy, G. *J. Am. Chem. Soc.* **1979**, *101*, 6710–6716.

(19) We proved the steric course of Tietze's and Görlitzer's transformation[10] (*Z*)-**10a** + AD-mix α → (−)-(2*S*,3*R*)-**11a** (Scheme 4, top) by establishing that the enantiomeric product (2*R*,3*S*)-**11a** (preparation: Scheme 6, top) was dextrorotatory: (−)-(2*S*,3*R*)-**11a** (82% *ee*) showed $[\alpha]_D^{20} = -20.0$ ($c = 1$ in $CHCl_3$) while (2*R*,3*S*)-**11a** (92% *ee*) showed $[\alpha]_D^{20} = +22.3$ ($c = 0.37$ in $CHCl_3$).

(20) The facial selectivity of the functionalizations of (*Z*)-**10a,b** with AD-mix α (Scheme 4, top[9]) lacked experimental support. The resulting diols were Sonogashira-coupled to provide diols[9] **13a**,**b** with the same *relative* configurations as the ones obtained from (*Z*)-**12a**,**b** and AD-mix α in one step (Scheme 4, bottom[10]). However, differently than the authors believed (ref 10 and footnote 2 therein) no specific rotations were measured on the Sonogashira route (ref 22b). This left the *absolute* configuration of these specimens of (−)-*ul*-**11a** and (−)-*ul*-**b** unproved.

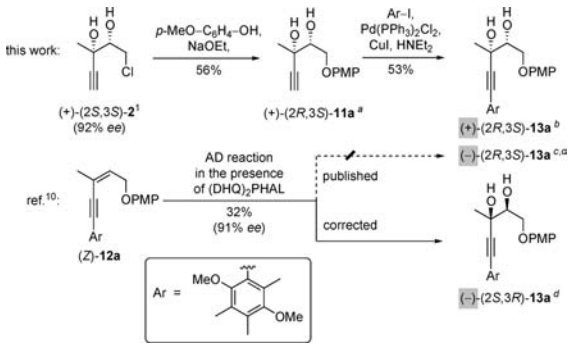
(21) Procedure: Gandolfi, C. A.; Di Domenico, R.; Spinelli, S.; Gallico, L.; Fiocchi, L.; Lotto, A.; Menta, E.; Borghi, A.; Rosa, C. D.; Tognella, S. *J. Med. Chem.* **1995**, *38*, 508–525.

(22) (a) The 3D structure of the dihydroxylation product (−)-("2*R*,3*R*")-**11a** should have emerged from the X-ray analysis of crystals of the monosulfonate derived with (+)-camphorsulfonyl chloride.[9] The ORTEP plot depicted the compound as **14** (ref 22b, p 72), but the corresponding valence formula was flawed as **15** (ref 22b; p 70) and published as such.[9] (b) Görlitzer, J. *Dissertation*, Universität Göttingen, 1997.



(23) (a) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970. (b) Sharpless, K. B.; Amberg, W.; Beller, M.; Chen, H.; Hartung, J.; Kawanami, Y.; Lübben, D.; Manoury, E.; Ogino, Y.; Shibata, T.; Ukita, T. *J. Org. Chem.* **1991**, *56*, 4585–4588. (c) Reference 2b. (d) Kolb, H. C.; Andersson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 1278–1291. (e) Vanhessche, K. P. M.; Sharpless, K. B. *J. Org. Chem.* **1996**, *61*, 7978–7979. (f) Fristrup, P.; Tanner, D.; Norrby, P.-O. *Chirality* **2003**, *15*, 360–368.

Scheme 6. AD Reactions Reassigned II: Proof That (*Z*)-**12a** and AD-Mix α React Differently than Published



[a] $[\alpha]_D^{20} = +22.3$ ($c = 0.37$ in $CHCl_3$). [b] $[\alpha]_D^{20} = +13.6$ ($c = 0.33$ in $CHCl_3$). [c] Compatibility of this sense of the specific rotation with the depicted configuration is excluded by our work. [d] $[\alpha]_D^{20} = -12.6$ ($c = 1.0$ in $CHCl_3$).

According to Scheme 6 chlorodiol (2*S*,3*S*)-**2**[1] was converted via its PMP-ether (2*R*,3*S*)-**11a**[21] and a Sonogashira coupling with 1-iodo-2,5-dimethoxy-3,4,6-trimethylbenzene into the dextrorotatory diol (2*R*,3*S*)-**13a**. Diol **13a** prepared from the arylated PMP-ether (*Z*)-**12a** and AD-mix α was levorotatory[10] and hence (2*S*,3*R*)-configured.

In summary it has been shown that *all* heterosubstituted (*E*)- and (*Z*)-methylpentenynes, which have been *vic*-dihydroxylated to date under the influence of DHQ-containing ligands are attacked as if preferring a "Sharpless/Norrby orientation" in any of the Sharpless-mnemonic transition states[23] **16**−**19** (Figure 1) such that steric hindrance in zone 1, which is (the most) repulsive, is minimized.

With respect to alkenes containing a trisubstituted C=C bond we reduced the number of "Chapleur oriented"[24] AD substrates by (*E*)-**10a**−**d** and (*Z*)-**12a**,**b**. When/if one does not accept the revised configuration[25] of the diol produced from isobutyl angelate and AD-mix *β*,[26] this implies a "Chapleur orientation" **20**[25] (Figure 1) in the transition state,[27−29] the only AD reaction affecting a "Chapleur oriented" trisubstituted C=C bond, of which we are aware may concern an α-alkylidenelactone.[30] It seems reasonable, accordingly, to base synthetic planning entailing an AD of a trisubstituted C=C bond on "Sharpless/Norrby orientations" **16**−**19** of the substrate and to specify that the sp^2-bonded H-atom shall be in the (most) hindered position (1).

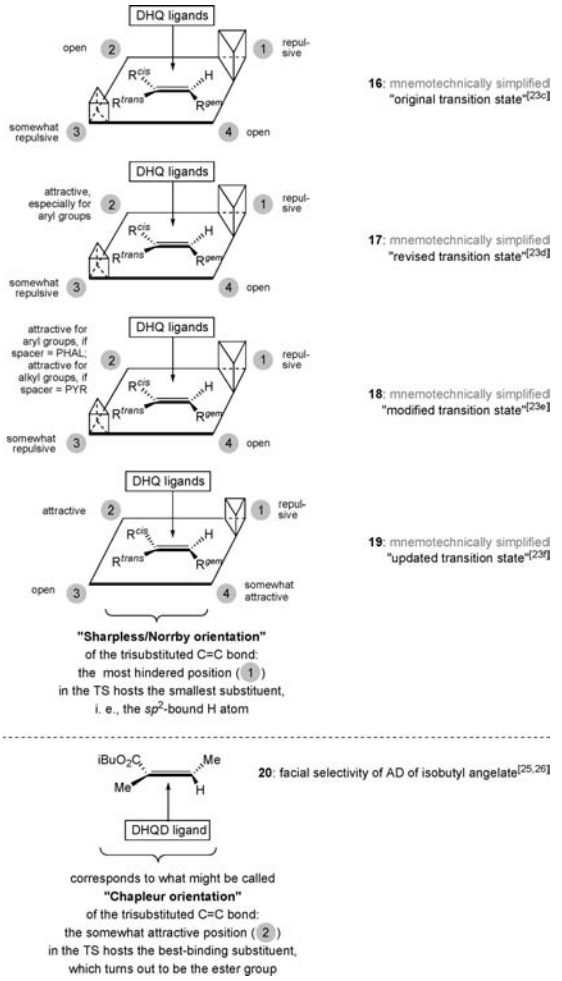


Figure 1. Stereoselectivities of ADs of standard substrates with a trisubstituted C=C bond in the presence of DHQ-containing ligands (top; DHQD-containing ligands attack from downside) and of isobutyl angelate in the presence of $(DHQD)_2PHAL$ (bottom).

Acknowledgment. The authors thank Dr. Thomas Netscher (DSM, Basel) for donations of (*E*)- and (*Z*)-3-methylpent-2-en-4-yn-1-ol.

Supporting Information Available. Experimental procedures, characterization data, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) A "Chapleur orientation" in the transition state of an AD represents the optimum of maximized bonding in zone 2 and minimized strain in zone 1.[25]

(25) Moitessier, N.; Henry, C.; Len, C.; Chapleur, Y. *J. Org. Chem.* **2002**, *67*, 7275–7282.

(26) Shao, H.; Rueter, J. K.; Goodman, M. *J. Org. Chem.* **1998**, *63*, 5240–5244.

(27) (a) Menthyl angelates undergo ADs with stereoselectivities matching "Sharpless/Norrby orientations" in the transition state: Torres-Valencia, J. M.; Cerda-García-Rojas, C. M.; Joseph-Natan, P. *Tetrahedron: Asymmetry* **1998**, *9*, 757–764. (b) The same is true for disubstituted angelates: Nicolaou, K. C.; Yue, E. W.; La Greca, S.; Nadin, A.; Yang, Z.; Leresche, J. E.; Tsuri, T.; Naniwa, Y.; De Riccardis, F. *Chem.—Eur. J.* **1995**, *1*, 467–494.

(28) (a) AD stereoselectivities of monocarbamoylated alkyl angelates in line with "Sharpless/Norrby orientations" in the transition state but without proofs: Claudel, S.; Olszewski, T. K.; Mutzenardt, P.; Aroulanda, C.; Coutrot, P.; Grison, C. *Tetrahedron* **2006**, *62*, 1787–1798. (b) dto. regarding ADs of a mono- and a dimethylated ethyl angelate: Stritzke, K.; Schulz, S.; Nishida, R. *Eur. J. Org. Chem.* **2002**, 3884–3892.

(29) The diols from AD-mix α and 2-(trimethylsilyl)ethyl angelate (Liu, H.; Jensen, K. G.; Tran, L. M.; Chen, M.; Zhai, L.; Olsen, C. E.; Søhoel, H.; Denmeade, S. R.; Isaacs, J. T.; Christensen, S. B. *Phytochemistry* **2006**, *67*, 2651−2658) or a monosubstituted angelate [Xie, W.; Ding, D.; Zi, W.; Li, G.; Ma, D. *Angew. Chem.* **2008**, *120*, *2886*−2890; Xie, W.; Ding, D.; Zi, W.; Li, G.; Ma, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 2844−2848 (Supporting Information)] were drawn−without proofs−as if emerging from "Chapleur orientated" substrates.

(30) Curran, D. P.; Ko, S.-B. *J. Org. Chem.* **1994**, *59*, 6139–6141.