Tetrahedron Vol. 47, No. 12/13, pp. 2195–2210, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
Pergamon Press plc

ASYMMETRIC SHARPLESS EPOXIDATION OF DIVINYLCARBINOL. *erythro*-D- AND -L-4-PENTENITOLS BY HYDROLYSIS OF REGIOISOMERIC EPOXY-4-PENTENOLS[1,2]

VOLKER JÄGER,*[a] DETLEF SCHRÖTER,[a] and BERNHARD KOPPENHOEFER[b]

[a]Institut für Organische Chemie der Universität, Am Hubland
D-8700 Würzburg, FRG
[b]Institut für Organische Chemie der Universität, Auf der
Morgenstelle 18, D-7400 Tübingen 1, FRG

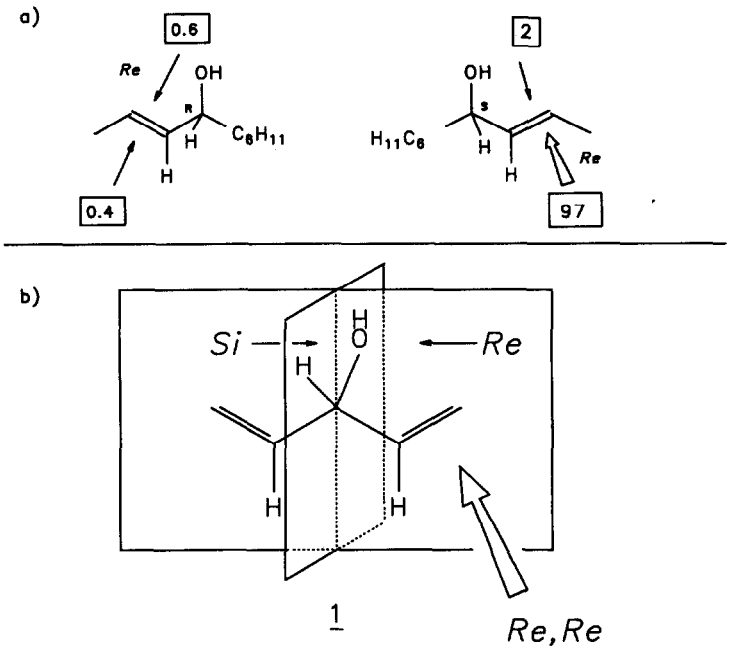
(*Received in Germany* 2 *January* 1991)

Abstract - The asymmetric Sharpless epoxidation of divinylcarbinol (**1**), a secondary, achiral allylic alcohol, is described in detail. The epoxidation proceeds with high enantio-control and diastereo-selection. The resulting 1,2-epoxy-4-pentene-3-ols **2** are equilibrated to afford the internal epoxides **5**. Hydrolysis of the regioisomers **2** and **5**, respectively, furnishes opposite enantiomers of *erythro*-4-pentenitols **3** with high selectivity. Several derivatives of **3** are described, as well as results of a less stereoselective route - from D-glyceraldehyde acetonide (**10**) - providing NMR data of the *threo* series. - The acute toxicity of divinylcarbinol (**1**) is reported, along with the mutagenicity of **1**, L-**2** and L-**5** as determined by Ames tests.

INTRODUCTION

The asymmetric epoxidation of primary allylic alcohols[3] and its extension to the kinetic resoluton of racemic, secondary substrates,[4] both discovered by Sharpless and coworkers, have seen rapid and extensive application in organic synthesis.[5] *Inter alia*, this approach has become attractive for the synthesis of common and rare carbohydrates, polyols, products of the arachidonic acid metabolism, and related fragments of many other natural products.[5,6] To the asymmetric Sharpless epoxidation mostly achiral, primary allylic alcohols, undergoing enantio-face differentiation,[7] have been submitted. The secondary ones used - heretofore chiral - respond to kinetic resolution, if racemates are submitted.[4,5e,5f] The true selectivity, namely exact data on the relative reactivity of the four diastereotopic π-faces in the tartrate-loaded titanium complex, has been determined, f.e., with separate enantiomers of cyclohexyl propenyl carbinol and the L-(+)-diisopropyl tartrate system.[4] Normalized, these numbers show a face selectivity ratio of 97 : 2 : 0.6 : 0.4, see Scheme 1.

Based on this, when erythro-L-4-pentenetriol L-**3** and related diols were required for studies of stereoselection in cycloadditions, we conceived divinylcarbinol (**1**) as a suitable precursor and a novel, intriguing substrate for asymmetric epoxidation.[2,8-10] Similar to the above pair of enantiomers, **1** incorporates two pairs of stereo-heterotopic π-faces, but now in one achiral structure. With L-(+)-tartrate mediators, **1** was expected to be epoxidized from the Re,Re-face preferentially (see Scheme 1), and from the Si,Si-face with the D-(-)-system which indeed turned out to be the case.[1,2,8-11]



Scheme 1. (a) Reported[4,5e] reactivity of stereo-heterotopic π-faces of a chiral, secondary allylic alcohol pair in the asymmetric Sharpless epoxidation mediated by L-(+)-diisopropyl tartrate, and (b) projected[1b,2] preferential Re,Re-attack in the case of achiral, secondary divinylcarbinol (1) with the L-tartrate system.

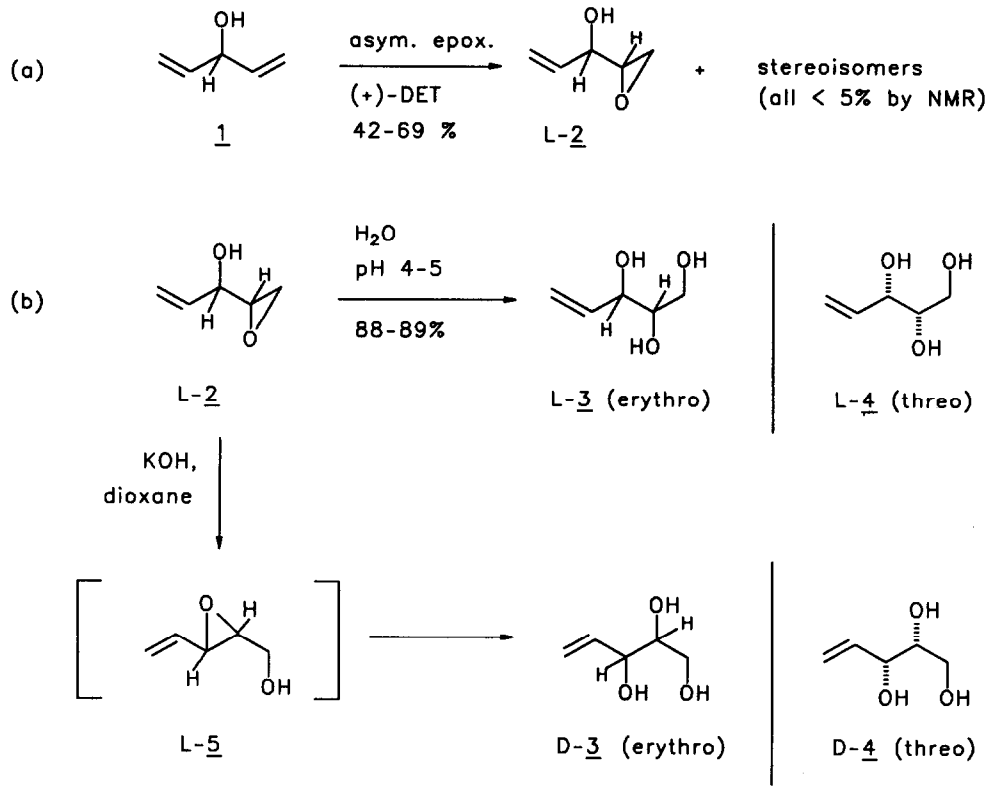
In the following we detail our results concerning the epoxidation of 1, the first substrate of this kind to be submitted to the Sharpless reaction.[1,2,8-11] It also deals with attempts to hydrolyze the resulting epoxypentenols 2 to obtain the desired pentenetriols 3 without stereo-diversion caused by the epoxy alcohol rearrangement. Finally, the results of our studies to secure the isomer composition, the relative and absolute configuration of the triols by classical methods, are presented.[2b] This includes glyceraldehyde-based efforts to secure authentic threo stereoisomers of these triols; an alternate route starting from D-ribonolactone has been detailed separately.[12]

ASYMMETRIC EPOXIDATION OF DIVINYLCARBINOL AND EPOXYPENTENOL HYDROLYSIS WITH RETENTION

Divinylcarbinol (1) was prepared from acrolein and excess vinylmagnesium bromide as described.[13] The dienol 1 was submitted to asymmetric epoxidation according to both procedures advanced by Sharpless et al., that is (i) stoichiometric[5,14] [ratio of L-(+)- or D-(-)-dialkyl tartrate/titanium tetraisopropoxide/tert-butyl hydroperoxide 1.2:1.0:2.0] and (ii) catalytic[15] [0.12:0.10:1.5, with 4 Å molecular sieve added]. The reactions were stopped when TLC monitoring showed complete consumption of 1 [(i) 26 to 45 h; (ii) 5 to 8 d, see Experimental].

The work-up of low-weight, water-soluble epoxidation products for long has been a problem[3] overcome only recently[15,16], cp. the glycidol case.[16] This seemed even more complicated with the divinylcarbinol epoxidation product 2 since we expected this to be rather sensitive towards acid- and base-induced hydrolysis (to give a water-miscible triol, vide infra), and further to be prone to base-catalyzed epoxide rearrangement (vide infra). Indeed, the latter side-reaction was encountered by us[2,9] and others.[10,11b] Fortunately, a procedure similar to the shortened

work-up of Oehlschlager et al.[6a] (conceived for distillable epoxyalcohol products) proved satisfactory.[2] Thus, the epoxypentenol **2** was obtained, after Kugelrohr distillation, in yields of 55-65%, as a mixture with 20-60% of tert.-butanol/tert.-butyl hydroperoxide.[2] The latter proved difficult to remove, but fractional distillation at last gave 42 to 45% of L-**2**, of 92-99% epoxy pentenol content (see Scheme 2a). Gratifyingly, in our hands this material showed a higher specific rotation[2] than that reported elsewhere.[10,11a,11m] With increasing routine yields of 60-70% of material with 92-99% epoxide content were obtained more recently using the catalytic version.[17]



Scheme 2

The product yield of **2** remained in the same range regardless of the version used, that is with (+)- or (-)-DET or (+)-DIPT. The resulting 1,2-epoxypentenol **2** was obtained as a single diastereomer according to ^{13}C NMR (*erythro/threo* >95:5). Attempts to determine the precise diastereomer ratio of **2** by capillary GC on chiral stationary phases were not successful[2b] (vide infra).[§]

The hydrolysis of L-**2**, when carried out on the crude mixture of epoxide(s)/TBHP/t-butyl alcohol with potassium hydroxide in aqueous dioxane[2,8], did not furnish the expected enantiomer L-**3** as the main *erythro*-triol product. The

§ Note added in proof (Dec. 1990): In recent full papers by Schreiber et al.,[18] who have taken up the divinylcarbinol (**1**) epoxidation, experimental procedures and data were reported. In connection with a mathematical model to describe this kind of process, and from analyses based on Mosher ester derivatization, it was concluded that "products with extraordinary levels of enantiomeric purity" had resulted; for **2** optical rotations of $[\alpha]^{23}_D$ = + 48.8°, c = 0.73, $CHCl_3$, and $[\alpha]^{21}_D$ = -46.4°, c = 1.15, $CHCl_3$, were given. This is in contrast to our results, with $[\alpha]_D$ values up to 61° (see Experimental).

NMR spectra showed the presence of a single diastereomer - *erythro*. The specific rotations of such triol samples (+18.0 to +21.7) were compared to that of authentic D-3 obtained from D-ribonolactone (+27.6), and this indicated that 80-90 to 20-10 mixtures of D-3/L-3 had been obtained. The first step should not have defied the plan, contradicting the many known and consistent results on the steric course of asymmetric epoxidation. We concluded therefore that the startling switch from the L- to the D-series must have been due to two inversions, at C-2 and C-3: first, by base-initiated 1,2 - 2,3-epoxide rearrangement, with inversion at C-2, and second, by hydroxide attack at C-3.

Indeed, less basic conditions for the hydrolysis - sodium carbonate in aqueous DMSO at 80° - gave a triol sample with the correct sign but still too low value ($[\alpha]_D^{18} = -12.7°$). Triol products with more negative rotation were isolated when the crude epoxide/t-Bu(O)OH mixture was directly hydrolyzed with water. Optimized conditions - pH 3-4 adjusted with acetic acid, 60° - gave the triols in high yield as spectroscopically pure oils (d.r. >95:5). The specific rotations of the various samples of L-3 [from the L-(+)-DET- and -DIPT-mediated epoxidations] were in the range of -24.2° to -28.4°, compared to $[\alpha]_D^{18} = +27.6°$ found for authentic D-3 from D-ribonolactone.[2,12]

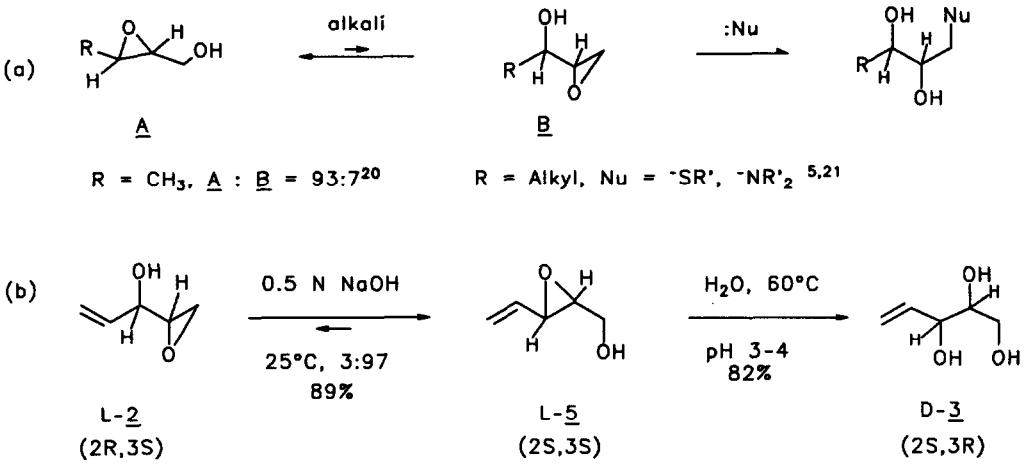
The relatively low values of optical rotation, obtained from these hygroscopic, viscous oils were not considered reliable. Fortunately, high precision GC analyses on capillary columns coated with D- and L-Chirasil-Val, respectively, became available, as detailed recently.[2b] These revealed that the main isomer, the *erythro*-L-pentenetriol L-3, constituted ca. 94% of the mixtures, with ca. 4% of the enantiomer D-3, and ca. 3.7/0.2 to 0.5% of the *threo*-pentenetriol enantiomers L-/D-4. The reference samples to identify the *threo* (and *erythro*) isomers were obtained from D-glyceraldehyde (see below) and, as mentioned above, from D-ribonolactone.[2,8,12]

EPOXYPENTENOL REARRANGEMENT AND HYDROLYSIS WITH TWO-FOLD INVERSION ("ENANTIOMERIZATION")

In the preliminary papers[2a,8] we suggested the interim formation of the internal epoxide L-5 and subsequent opening by hydroxide ion at C-3, to account for the L-2 → D-3 formation observed. Epoxide 'migrations' of this kind were first encountered with anhydropyranoses;[19] they were systematically investigated by Payne[20] in 1962 and have more recently become a key feature of several synthetic applications of the A.S.E. process.[5,21] For example, trans-2,3-epoxy alcohols, on joint action of equilibrating alkali and strong(er) nucleophiles, give 1-substituted 2,3-diols through attack at the terminal carbon atom of the 1,2-epoxide,[5,21] although this is present only in a few percent.[20] Clearly, the reactivity sequence is 2° << 1° (Scheme 3a).

This reactivity order was preserved in the hydrolysis of the 1,2-epoxypentenol L-2 in weakly acidic medium, under non-equilibrating conditions as described above.[1,2,8] On action of base, equilibration of 2 should favour the presumed 2,3-epoxide 5, and lead to a situation with three potential sites for nucleophilic attack: C-5 (S_N2' attack) and the two 2° epoxide carbon atoms of which the allylic one (C-3) in 5 might effectively compete with C-1 of 2.

Indeed, NMR experiments with L-2 in D_2O/NaOD showed that the rearrangement took place gradually at 0 °C, with ca. 77% conversion after 45 minutes and ca. 90% after 2 hours. At room temperature the equilibrium mixture of 3:97 was reached after 30 minutes and the new product was identified as trans-2,3-epoxy-4-pentenol 5. The trans configuration followed from the coupling constant $J_{2,3} = 1.7$ Hz; the absolute configuration of 5 was deduced as L (2S,3S) from the well-established course of the general reaction and the result of subsequent hydrolysis (vide infra). In preparative runs L-5 was isolated in 89% yield, contaminated with 3% of the positionally isomeric educt L-2.[9,22] As expected, the like results were encountered in the D-series [D-2 produced with D-(-)-tartrate mediators].



Scheme 3

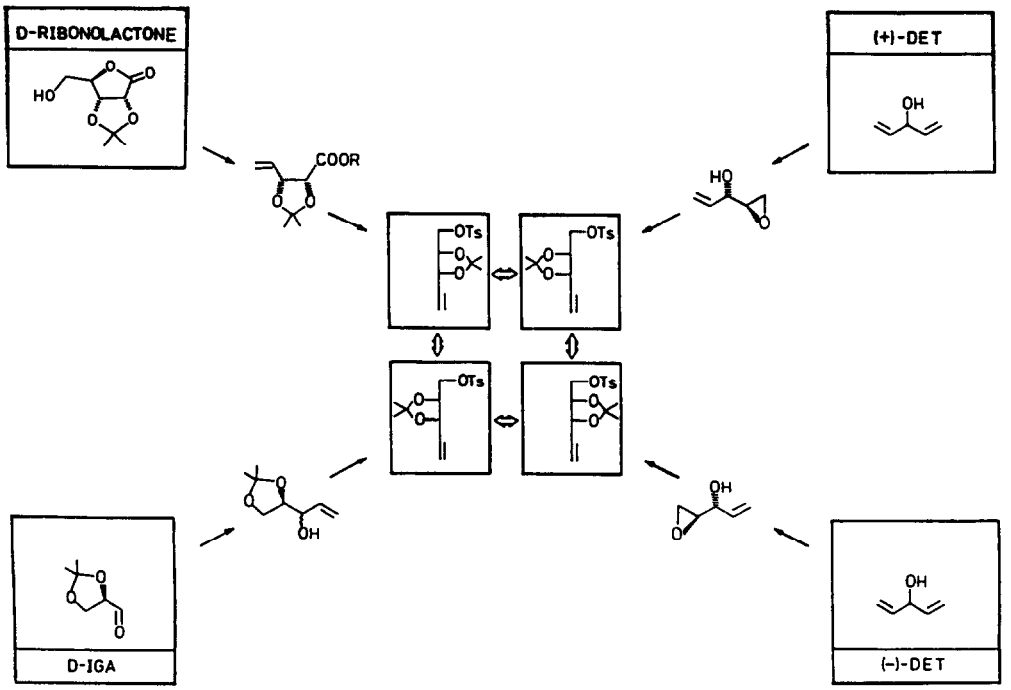
The 2,3-epoxypentenols **5** were hydrolyzed at pH 3-4 as above, and again the pentenetriols **3** were isolated in high yield and diastereomer purity (>95:5 by ^1H and ^{13}C NMR). Thus, samples of the *erythro*-triol D-**3** were obtained by the sequence **1**→L-**2**→L-**5**→D-**3**, with specific rotations of $[\alpha]_D^{18} = +23.5°$ and $+24.2°$. This indicates a ca. 94:6 e.r. when compared to the value of the reference sample from D-ribonolactone ($+27.6°$; >99.8% pure).[2,12] Again, GLC on D-/L-Chirasil-Val gave more precise figures for the four stereoisomers: D-**3**/L-**3**/D-**4**/L-**4** = 93.3 : 4.2 : 1.3 : 1.2.[2b] For the *erythro* triols **3** this agrees well with the results of the direct route **1**→L-**2**→L-**3**, but not so with the amount and ratio of the *threo* isomers **4**. Experiments with enriched or pure *threo*-epoxypentenols **2** are warranted here, in order to determine the equilibrium with cis-**5**, the relative rates of hydrolysis, and also to quantify the kinetic resolution process following the epoxidation step.[11c] However, the synthesis of cis-**5** by asymmetric epoxidation may be troublesome as judged from the results of a related dienol epoxidation.[6a]

CYCLIC ACETALS FROM PENTENETRIOLS. ASSIGNMENT OF CONFIGURATIONS

In order to secure the configuration and isomeric purity of the DVC epoxidation/ hydrolysis products **2** - **5**, the pentenetriols were prepared independently starting from isopropylidene-D-glyceraldehyde (D-IGA) and D-ribonolactone as reported earlier,[1,2,8] see Scheme 4.

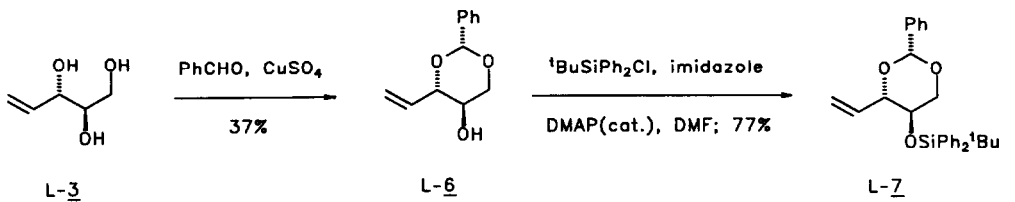
The former part is detailed below, plus the conversion of the triols **3** into cyclic benzylidene and isopropylidene acetals **6** and **9**, respectively. Of these, the tosyl acetonide **9** proved a suitable, crystalline relais compound to evaluate the stereochemical results of the different routes, cf. Scheme 4.

The 1,3-O-benzylidene acetal L-**6** was obtained from L-**3** in moderate yield (37%) and silylated to afford L-**7**, see Scheme 5. The dioxane structures of **6** and **7** are evident from the signals for C-2 and C-3 (4-pentenitol numbering), appearing at 65-67 and 83 ppm, and the triplet from C-1 at ca. 71 ppm, distinctly different from the values recorded for the dioxolans [9,11,12,14] (see Table 2). Likewise, the proton couplings $J_{1c,2}$ found in L-**6** and L-**7** are in the range characteristic for di-axial H and di-equatorial OH(siloxy)/vinyl group arrangements in chair conformations (see Table



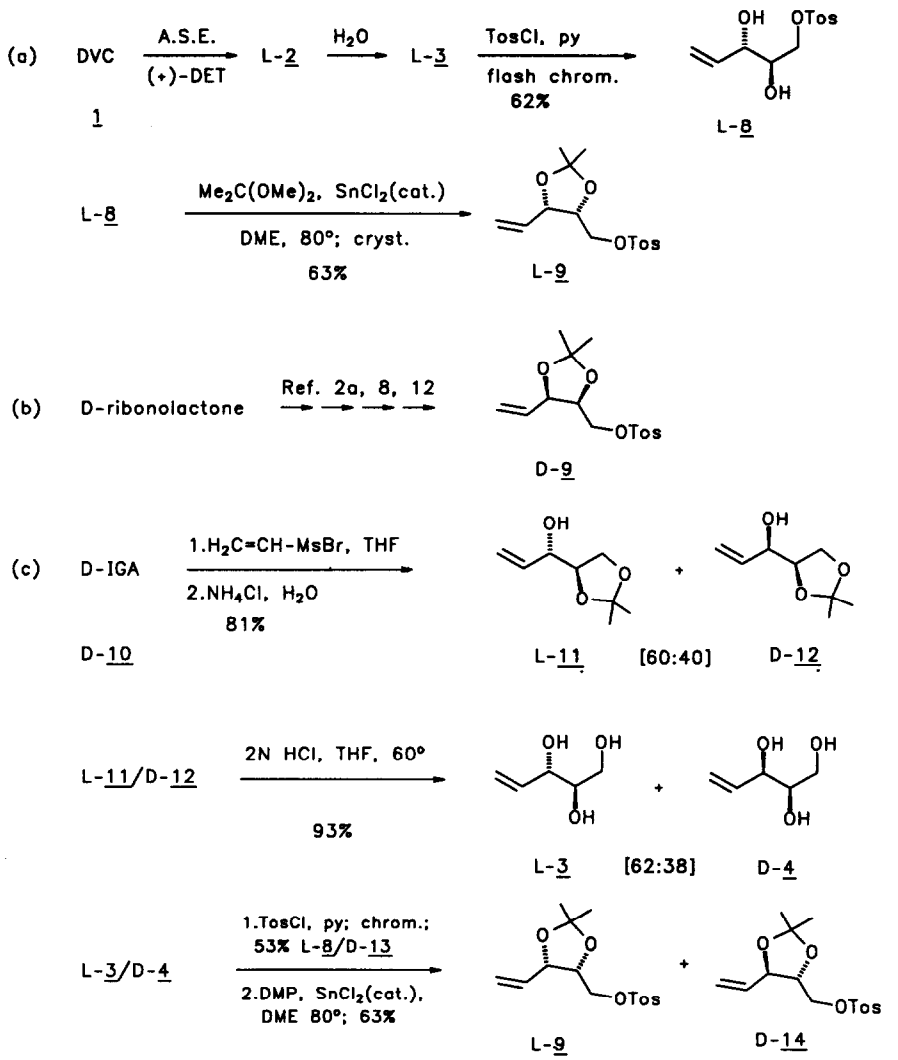
Scheme 4

1). This confirms the *erythro* configuration of L-**6** and L-**7** as well as that of the precursor L-**3**. - The vinyl dioxanes L-**6** and L-**7** were employed later in studies concerning transition state conformations of nitrile oxide cycloadditions.[9]



Scheme 5

The tosyl acetonide L-**9** was prepared via the triol L-**3** and the monotosylate L-**8** as shown below [Scheme 6(a)]. According to NMR only one diastereomer was present (d.r. >95 : 5), and the melting point of L-**9** agreed well with that of D-**9** obtained from D-ribonolactone.[2a,8] From the comparison of optical rotations $[\alpha]_D^{20} = +42.5°$ (c = 0.57, $CHCl_3$) for L-**9**, -44.5° (c = 1.87, $CHCl_3$) for D-**9** [Scheme 6 (b)], the enantiomer ratio for the sample of L-**9** derived from DVC **1** amounted to ca. 98 : 2. The difference to the results of CGC analyses at the stage of the triols **3** [92.2 : 3.9 : 3.7 : (0.2-0.5)[2b], see above] is minor and not unexpected, since chromatography and crystallization had been applied on the way to L-**9** (see Experimental Part).

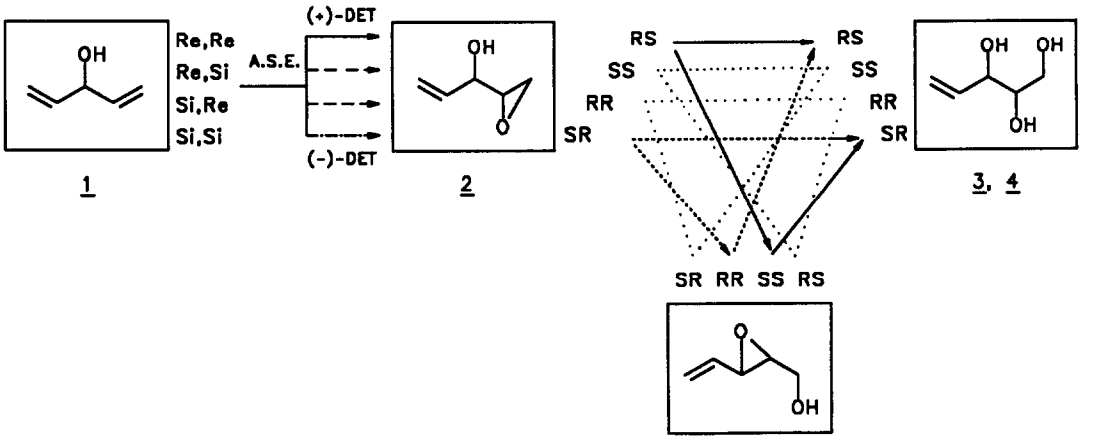


Scheme 6. Tosyl acetonides L-**9**, D-**9**, and D-**14** from (a) DVC epoxidation, (b) D-ribonolactone, and (c) from D-glyceraldehyde acetonide D-**10**.

The synthesis of L-**3** and L-**9**, starting from D-glyceraldehyde acetonide (D-IGA) **10**, was less satisfactory.[2a,8] The addition of vinylmagnesium bromide in THF gave mixtures of the *erythro* and *threo* acetonides **11** and **12**, ranging from d.r. 60:40[23a] (no additive) to 75:25 (zinc chloride[23b] added). In the latter case, substantial racemization was witnessed when the product mixture was carried through to the relais stage of the crystalline tosyl acetonide **9**. With the former case *no* racemization of D-10 had occurred; this was shown by hydrolysis of the ca. 60:40 mixture of **11**/**12** and CGC analysis of the resulting mixture of triols **3**/**4**[2b] (see Scheme 6). As above, this mixture of enantiomerically pure diastereomers was transformed into the tosyl acetonides L-**9**/D-**14** via the monotosylates L-**8**/D-**13**. Thus, the NMR data of threo series - D-**4**, D-**12**, D-**13**, D-**14** - were accessible also, to facilitate and confirm the assignment of structures and configurations of both series.

CONCLUSION

The pentenetriol syntheses from divinylcarbinol (1) presented here offer a dual system of stereocontrol which is summarized in Scheme 7. Epoxidation of **1** with the respective tartrate mediator furnishes one or the other enantiomer of the *erythro*-1,2-epoxypentenols **2**. Direct hydrolysis affords the triol enantiomers L- and D-3 selectively (2R,3S and 2S,3R), while the detour via the trans-2,3-epoxypentenols **5** leads to the opposite enantiomers of **3**, with similarly high e.r. The stereochemical course of events is illustrated in Scheme 7.



1 2 3, 4 5

Scheme 7

The disclosure of the DVC epoxidation in 1985/86[2,8,10] has initiated both extensions of the concept and applications of these and derived building blocks in synthesis;[11,22] many more are easily predicted. Currently, we are concentrating on studies of the fundamental reactions of the unique epoxide pair **2**/**5**.[9,11j,11k] This should make available many versatile, optically active C_4 to C_6 building blocks with high (stereo)selectivity;[§] conceptually, the search for novel, intriguing cases of regio- and stereo-control[£] in this series seems both fascinating and promising.[9,11j-11m]

The use of substrates as exemplified by DVC **1** - enantiotopic ligands (alkenyl, acyl; alkyl) attached to a prostereogenic ("prochiral") sp^3-atom, thus containing diastereotopic faces or groups - in reactions with chiral

---

§ Concerning reactions that give rise to unequal mixtures of (stereo)isomers we use the term 'selective', 'selectivity', etc (and d.r., e.r., r.r. numbers[24]). The classical definition of E.L. Eliel (in: *Stereochemistry of Carbon Compounds*, p.436ff., MacGraw Hill and Kogakusha Co., New York/Tokyo 1962) concerning 'stereoselective'/'-specific' processes - widely used - was already deemed "not perfect" by its author. The case of 'stereospecific' reactions with Z/E-alkene pairs, being (only) 'stereoselective' with small ring examples of non-accessible E-alkenes, was cited then. The term 'stereospecific' is further misleading when reactions of chiral compounds are considered: If the stereogenic centre(s) is (are) not touched, any derivatization of - let's say - 2-butanol would be 'stereospecific', and likewise, any reaction of D-glucose, cholesterol and so on.

£ We propose to use 'control' in the sense defined by common dictionaries:"Power of directing, command" (*The Concise Oxford Dictionary*, 6th ed., p. 221, At the Clarendon Press, Oxford 1976). If a reaction may lead to two (or more) products, and one is obtained only or predominantly, this may hardly be called 'controlled'. The use of the term 'control' should be restricted to cases where one has found means to generate one and the other product(s) with high selectivity each. The asymmetric Sharpless epoxidation, f. e., is regarded as genuine case of enantio-control.

agents of high stereo-differentiating ability has some precedence. E.g., the potential of enzymes for the selective conversion of bifunctional substrates with several prostereogenic centres into products with one highly enriched enantiomer has widely been recognized.[25,26] Still, reports on non-enzymic, 'chemical' processes of this kind are rare, and substrates with several prostereogenic centres suitable to such transformations with enantiomerically pure reagents have remained few.[27,28]

In this respect it is interesting to note that many enzyme-catalyzed conversions of "prochiral" substrates (with several pro-enantiogenic and/or pro-diastereogenic centres[29,30]) head under "enantiotopos" differentiation, which is correct with regard to educt/substrate relations. In many of these cases - the hydrolysis of 3-hydroxy-3-methyl-glutaric acid (HMGA) diesters be taken as a typical example - the enantiotopic groups present *diastereo-faces*, like those met with divinylcarbinol (1). It would be highly interesting to learn, although difficult to verify experimentally, if enzymes discriminate diastereo-faces when hydrolyzing one of two enantiotopic ester ligands with high "enantio-selectivity". "Stereochemically cryptic", a term introduced by Hanson and Rose,[31] adequately characterizes the present state of our knowledge in this area.

EXPERIMENTAL

General

M.ps (Tottoli apparatus, Büchi SMP-20) and b.ps/ranges are uncorrected; if not stated otherwise, b.p./b.r.(boiling range) refers to the air bath temp of Kugelrohr distillation. IR spectra: Beckmann Akkulab 4; NMR spectra: Bruker WM 400 or Bruker AC 200; TMS as internal standard, d(TMS)= 0 ppm. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter using the Drude method. Flash chromatography was carried out on Silica (Woelm, 32-63 μm), TLC on silica-coated alumina sheets (Merck, Si60 F254), detection by UV (254 nm) or phosphomolybdic acid spray reagent (10% in ethanol)/heat gun treatment. Capillary GC analyses were carried out on Chirasil-Val-coated columns at Tübingen, see lit.[2b] Solvents were dried before use; air- and moisture-sensitive reactions were carried out in flame-dried glassware. Anhydrous t-butyl hydroperoxide was prepared from a 70% commercial soln as described by Sharpless et al.[14] $Ti(OiPr)_4$ (Aldrich) was distilled before use; the L-(+)-DET, D-(-)-DET, and L-(+)-DIPT samples used were purchased from Janssen, Aldrich, and Merck-Schuchardt.

Toxicity, mutagenicity, and handling of divinylcarbinol (DVC; 1) and epoxypentenols L-2 and L-5

Divinylcarbinol (1) was marketed recently (Aldrich Chemical Co., Milwaukee/USA; Fluka Chemie AG, Buchs/Switzerland); however, only general safety data are provided. More specific studies[32] showed for
(i) DVC 1: a) acute toxicity towards mice (NMRI,), po: up to 100 mg/kg - (negative); ip: lowest killing dose ca 75 mg/kg (4 specimen; doses of 30, 50, 75, 100 [mg/ kg]); b) Ames tests negative (with TA 100-S9 and TA 100 S9);
(ii) L-*erythro*-1,2-epoxy-4-pentene-3-ol (L-2): Ames test +, 220 rev./μmol;
(iii) L-*threo*-2,3-epoxy-4-pentenol (L-5): Ames test +, 60 rev./μmol.
For comparison: ethyl-oxirane 40, acetoxy-oxirane 6120 rev./μmol.[33]

In earlier tests with rabbits concerning acute dermal toxicity of 1 high activity has been registered (approximate average lethal dose <200 μl/kg).[34] The *handling precautions* we have observed in working with these compounds since 1984, and that we recommend, are: all operations be performed in a well-ventilated, closed hood with disposable gants; a close-by $KMnO_4$ bath in which all contacted glass-ware etc. be immersed right after use. Of course, inhalation or skin contact should strictly be avoided.

Starting materials

Divinylcarbinol (1) was prepared from vinylmagnesium bromide (66.9 g, 0.510 mol) and acrolein (23.6 g, 0.420 mol) in THF/ether (4:1) at -15°.[13] After aqueous work-up 1 was obtained by fractional distillation; 22.4 g (64%), b.p. 116°/760 Torr (lit[13] 55%, 115-116°/760 Torr); NMR data see Tables 1,2.

(R)-2,3-O-Isopropylidene-glyceraldehyde (10): Prepared from D-mannitol bis-acetonide according to Pfander and Dumont,[35] using K_2CO_3 in place of Na_2CO_3;[36] 50 mmol-scale, 77%, b.p. 39-45°/15 Torr, pure by ^1H NMR (lit[33] 81%, 39°/15 Torr).

Asymmetric epoxidation of divinylcarbinol (1)

(2R,3S)-1,2-Epoxy-4-pentene-3-ol (L-2) by (+)-DET-mediated epoxidation of 1: Under nitrogen abs. CH_2Cl_2 (1400 ml) was cooled to -30°, then 55.5 ml (186 mmol) of titanium tetraisopropoxide and 46.0 g (224 mmol) of L-(+)-diethyl tartrate were added sequentially following a procedure of Sharpless et al.[3,4,14] After stirring for 15 min, 1 (15.6 g, 186 mmol) and a CH_2Cl_2 soln of t-butyl hydroperoxide (3.15 M; 118.3 ml, 372.8 mmol) were added and the mixture kept in a freezer at -27° for 130 h. The reaction was monitored by TLC (ethyl acetate/p.e. 1:1; phosphomolybdic acid; R_f 0.5 for 1 and 0.3 for 2) and stopped when the spot from DVC 1 had disappeared.
The soln was warmed to -10° and, with vigorous stirring, was quenched with 200 ml of 30% aqueous tartaric acid. Stirring was continued for 15 min at 0°, then the layers were separated. The water phase was extracted with ether (3 x 100 ml) and the combined organic solutes were dried (Na_2SO_4) and concentrated. The remainders were distilled through a 25cm-Vigreux column to give 8.50 g of a colourless liquid, consisting of 2 with 3% t-butyl hydroperoxide or t-butyl alcohol (from ^1H NMR); other signals (of the *threo* diastereomer) could not be detected (< 5%). Corrected yield of L-2 8.20 g (45%), b.p. 70-72°/16 Torr. A similar run, after distillation, gave 29% of L-2 with 99% purity (1% TBHP), from which the following data were recorded; $[\alpha]_D^{22}$ = +61.1°(c = 2.31, $CHCl_3$; cf. lit[10] $[\alpha]_D^{22}$ = +46.7°(c = 1.38, $CHCl_3$); lit[11m] $[\alpha]_D^{24}$ = +48.0°(c = 2.76, $CHCl_3$). IR (film): 3600-3300, 3090, 2920, 2880, 1640, 1250cm^{-1}. ^1H, ^{13}C NMR data see Tables 1,2.

When the work-up was done by Kugelrohr distillation, mixtures of L-2 with 40-60% TBHP/t-BuOH were obtained (yield of L-2 53-67% from ^1H NMR integration), that were used as such in the hydrolysis step, vide infra.

L-(+)-DIPT version: Carried out as above, with 1 (5.21 g, 62.0 mmol), TBHP (2.0 equiv), $Ti(OiPr)_4$ (1.0 equiv), L-(+)-DIPT (1.2 equiv); 92 h at -17°. Yield of L-2: 2.47 g (40%) in fractions of 53 to 96% purity, b.r. 50-70°/16 Torr; ^1H NMR in accord with the data given above. The stereoisomer composition was assayed after hydrolysis by GC, vide infra.

Catalytic version: Following the Hanson/Sharpless procedure[15] from 1 (25.00 g, 297 mmol), TBHP (1.38 equiv), $Ti(OiPr)_4$ (0.10 equiv), L-(+)-DET (0.12 equiv), molecular sieves (4 Å, 15 g) after 7 d at -25° TLC control (ethyl acetate/p.e. 6:4) showed almost complete reaction. After work-up as above, extraction with CH_2Cl_2 (5 x 40 ml) and fractionation by means of a 30cm-Vigreux column 22.10g L-2 (containing 8% TBHP/t-BuOH, corrected yield 69%) was collected; b.p.55-70°/21 Torr, $[\alpha]_D^{25}$ = +53.0°(c = 1.035, $CHCl_3$); from another run (43%, impurity 5%): $[\alpha]_D^{22}$ = +60.2°(c = 2.571, $CHCl_3$). NMR data as above, see Tables 1,2.

(2S,3R)-1,2-Epoxy-4-pentene-3-ol (D-2): Prepared as above from 1 (93.0 mmol), using the stochiometric A.E. procedure with D-(-)-DET and molecular sieves (3 Å) added, reaction time 119 h; fractions of 1.3 and 2.3 g (with 8 and 3% TBHP/t-BuOH, respectively); corrected yield of D-2 3.5 g (38%), b.p. 70-72°/16 Torr; $[\alpha]_D^{22}$ = -59.1°(c = 2.21, $CHCl_3$; from the sample with 97% purity). ^1H NMR data identical to those obtained for L-2; stereoisomer composition after hydrolysis see preparation of D-3. [Found for a sample of D-2 prepared catalytically with D-(-)-DIPT, $[\alpha]_D^{20}$ = -58.5° (c = 0.285, $CHCl_3$): C, 60.21; H, 8.30. Calc. for $C_5H_8O_2$ (100.1): C, 59.98; H, 8.05%.]

***Erythro*-4-pentene-1,2,3-triols L-3 and D-3 from hydrolyses of 1,2-epoxy-4-pentene-3-ols 2**

Hydrolysis of L-2 with base with partial enantiomerization to give L-3/D-3: 3.32 g of epoxide L-2, admixed with 60% of TBHP/t-BuOH (1.53 g of pure epoxide, 15.3 mmol) was put into a solution of KOH (7.70 g) in H_2O/dioxane (92/110 ml) and heated under reflux for 16 h. The mixture was neutralized with dilute HCl, concentrated *in vacuo* and taken up with ethanol. Filtration and rota-evaporation gave an oil which was dried over P_4O_{10} and distilled (Kugelrohr); 671 mg (38%) of a slightly yellow oil, b.r. 140-170°/ca. 0.1 Torr; $[\alpha]_D^{22}$ = +18.0°(c = 1.57, CH_3OH), GC analyses on L/D-Chirasil: (2R,3S)(L-3) 13.40/12.99, (2S,3R) (D-3) 84.50/84.59, (2S,3S) (L-4) 0.78/1.07, (2R,3R) (D-4) 1.32/1.35%.

Hydrolysis of L-2 in less basic medium (1.5 mmol of L-2; 30.0 mmol of Na_2CO_3 in 20 ml H_2O/DMSO 1:1, 5.5 h at 80°) and work-up by fractional distillation gave 51% of triols; colourless oil, b.r. 150-170°/0.1 Torr; $[\alpha]_D^{18}$ = +12.7°(c = 2.168, CH_3OH). GC on L/D-Chirasil-Val: (2R,3S) (L-3) 67.69/68.15, (2S,3R) (D-3) 27.81/27.32, (2S,3S) (L-4) 3.87/3.87, (2R,3R) (D-4) 0.63/0.66%.

(2R,3S)-4-Pentene-1,2,3-triol (L-3) by hydrolysis of L-2 at pH 3: A soln of the epoxide L-2 (2.00 g of a sample with 13% TBHP/t-BuOH); 1.73 g of pure epoxide, 17.3 mmol) in 50 ml of water was brought to pH 3 by addition of acetic acid and warmed to 60° for 68 h. The mixture was concentrated *in vacuo* to leave 2.07 g of a pale-yellow oil, which on Kugelrohr distillation at 140-160°/0.1 Torr afforded L-2 as a colourless, viscous oil (1.8 g, 88%; $[\alpha]_D^{18}$ = +24.2°(c = 1.485, MeOH). Analytically pure material was obtained after drying with 3 Å molecular sieves in ethanol and distillation as above; $[\alpha]_D^{18}$ = -25.8°(c = 1.39, MeOH). Similar runs (84-89% yield) gave material with rotations between -25.9° and -28.4°; GC composition of the latter sample on D/L-Chirasil-Val: (2R,3S) (L-3) 92.18/92.21, (2S,3R) (D-3) 4.02/3.88, (2S,3S) (L-4) 3.30/3.37, (2R,3R) (D-4) 0.50/0.54. IR (film): 3340 (b), 3080, 2980, 1220 cm^{-1}. ^1H, ^{13}C NMR data see Tables 1,2. [Found: C, 50.32; H, 9.00. Calc. for $C_5H_{10}O_3$ (118.1): C, 50.84; H, 8.53%.]

L-3 from L-2 [prepared by L-(+)-DIPT-mediated A.E. of 1]: 520 mg of L-2 [containing ca. 4% of TBHP/t-BuOH; 500 mg, 5.00 mmol of pure L-2, obtained from 1 with L-(+)-DIPT, *vide supra*] was hydrolyzed as above; yield after Kugelrohr distillation 530 mg (89%), composition 96% *erythro*-3 (L/D-3) and ca. 5% *threo* triols 4 (from ^{13}C NMR),

$[\alpha]_D^{18}$ = -26.3°(c = 2.345, CH_3OH). GC analysis on D-Chirasil-Val: (2R,3S) (L-3) 92.14, (2S,3R) (D-3) 2.13, (2S,3S) (L-4) 4.51, (2R,3R) (D-4) 1.22%.

(2S,3R)-4-Pentene-1,2,3-triol (D-3) by hydrolysis of D-2: As described above, from hydrolysis of 122 mg (purity 73%, rest t-BuOH; corrected 88 mg, 0.88 mmol of pure 2 from D-(-)-DET-mediated A.E. of 1) in 5 ml of H_2O at pH 3-4 (adjusted by adding acetic acid) and heating to 60° for 40 h; yield of D-3, after Kugelrohr distillation at ca. 170°/0.1 Torr, 80 mg (78%); colourless oil, $[\alpha]_D^{18}$ = +24.2°(c = 0.574, CH_3OH). GC analysis on L/D-Chirasil-Val: (2R,3S) (L-3) 4.01/3.79, (2S,3R) (D-3) 92.18/92.14, (2S,3S) (L-4) 0.17/0.20, (2R,3R) (D-4) 3.64/3.86%.

Rearrangement of the 1,2-epoxypentenols 2 to give 2,3-epoxypentenols 5 and hydrolysis of L-5:

(2S,3S)-2,3-Epoxy-4-pentenol (L-5) by rearrangement of 1,2-epoxide L-2: Crude L-2 (2.10 g, 95% pure, 1.99 g of epoxide; 19.9 mmol) was added to 20 ml of 0.5 N NaOH and stirred for 30 min at room temp. Extraction with CH_2Cl_2 (3 x 35 ml), drying of the combined organic phases (Na_2SO_4), and evaporation gave 1.78 g (89%) of a colourless, analytically pure oil that consisted of L-5/L-2 in a ratio of 97:3 (from ^1H, ^{13}C NMR): b.p. 72°/15 Torr; $[\alpha]_D^{22}$ = -57.1°(c = 1.68, $CHCl_3$); from another run: $[\alpha]_D^{22}$ = -56.2°(c = 2.555, $CHCl_3$). IR (film): 3600 - 3300(b), 3090, 2990, 2920, 2870, 1640(w) cm^{-1}. ^1H, ^{13}C NMR see Tables 1,2. [Found: C, 59.68; H, 8.21. Calc. for $C_5H_8O_2$ (100.1): C, 59.98; H, 8.05%.]

(2S,3R)-2,3-Epoxy-4-pentenol (D-5) by rearrangement of 1,2-epoxide D-2: Prepared as above from D-2 (1.00 g of 92% pure epoxide, 927 mg, 9.27 mmol); yield 850 mg of D-5 containing 3% of TBHP/t-BuOH and 3% of D-2 (corresponding to 800 mg, 86% of pure D-5); spectral data in complete agreement to those listed for L-5, see Tables 1,2.

D-3 from hydrolysis of 2,3-epoxypentenol L-5: A soln of the 2,3-epoxide L-5 (290 mg, 2.90 mmol, with 3% of L-3) in water was brought to pH 3 with acetic acid (6 drops) and warmed to 60°. After 18 h the solvent was removed under reduced pressure, the residue was dissolved in abs ethanol (20 ml) and dried over 3 Å molecular sieves. Kugelrohr distillation gave D-3 as a colourless, spectroscopically pure (d.r. > 92 : 8) oil; 280 mg, 82%; b.p. 160-170°/0.2 Torr; $[\alpha]_D^{18}$ = +23.5°(c = 2.93, MeOH). GC analyses on L/D-Chirasil-Val: (2R,3S) (L-3) 4.25/4.08, (2S,3R) (D-3) 93.10/93.63, (2S,3S) (L-4) 1.37/1.16, (2R,3R) (D-4) 1.28/1.13%. IR (film): 3700-3100, 2940, 2890, 1640, 1430, 1040 cm^{-1}. ^1H, ^{13}C NMR data in agreement with those of L-3 listed in Tables 1,2.

1,3-O-Benzylidene acetals from triol L-3

(2R, 3S)-1,3-O-Benzylidene-4-pentene-1,2,3-triol [(2R,4S,5R)-5-hydroxy-2-phenyl-4-vinyl-1,3-dioxane] (L-6) from triol L-3: A mixture of L-3 (300 mg, 2.54 mmol; from sample with $[\alpha]_D^{20}$ = -25.8°, see above), benzaldehyde (5 ml) and anhydrous $CuSO_4$ (200 mg, 1.25 mmol) was stirred at room temp. for 64 h. Water (20 ml) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 15 ml), the organic solutes combined, dried (Na_2SO_4), and evaporated. Excess benzaldehyde was removed by distillation (Kugelrohr; up to 80°/0.1 Torr) and the residue crystallized twice from benzene/p.e. and ether/p.e., to give colourless plates of pure L-6 (NMR); 190 mg, 37%, m.p. 87-90°; $[\alpha]_D^{20}$ = -57.0°(c = 1.46, $CHCl_3$). IR (KBr): 3440, 3090, 3040, 2970, 2910, 2870, 1395 cm^{-1}. ^1H, ^{13}C NMR see Tables 1,2. [Found: C, 70.06; H, 6.80. Calc for $C_{12}H_{14}O_3$ (206.2): C, 69.89; H, 6.84%.]

(2R,3S)-1,3-O-Benzylidene-2-O-(t-butyldiphenylsilyl)-4-pentene-1,2,3-triol [(2R,4S,5R)-5-(t-butyldiphenylsiloxy)-2-phenyl-4-vinyl-1,3-dioxane] (L-7) from L-6: To a soln of imidazole (395 mg, 5.80 mmol) and tert.-butyldiphenylsilylchloride (0.74 ml, 2.86 mmol) in DMF (3 ml) was added L-6 (460 mg, 2.2 mmol), dissolved in DMF (15 ml)/DMAP (15 mg, 0.10 mmol). After 5 d at room temp. the mixture was poured into ice-water (70 ml) and partitioned against CH_2Cl_2(3 x 40 ml). The extracts were washed with sat NH_4Cl (30 ml), $NaHCO_3$ (30 ml), and water (3 x 30 ml), dried over Na_2SO_4 and evaporated. The residue was crystallized from MeOH to give 760 mg (77%) of a colourless solid, L-7, m.p. 70-72° (with trace impurity according to TLC), from which an analytically pure sample was obtained by recrystallization from MeOH; m.p. 76-78°, $[\alpha]_D^{20}$ = -25.2°(c = 2.79, $CHCl_3$). IR (KBr): 3070, 3050, 2950, 1450, 1420, 1370, 1090, 1020 cm^{-1}. ^1H, ^{13} NMR, see Tables 1,2. [Found: C, 75.58; H, 7.38. Calc for $C_{28}H_{32}O_3Si$ (444.6): C, 75.63; H, 7.25%.]

(2R,3S)-2,3-O-Isopropylidene-1-tosylate L-9 from triol L-3

(2R,3S)-1-O-p-Tosyl-4-pentene-1,2,3-triol (L-8) from L-3: At 0° tosyl chloride (270 mg, 1.42 mmol) was added to a mixture of L-3 (140 mg, 1.19 mmol)/pyridine (0.30 ml, 3.7 mmol) in CH_2Cl_2 (7 ml) and kept at 0° for 6 d. The product soln was poured into ice-water (10 ml) and the aqueous phase extracted with CH_2Cl_2 (2 x 15 ml). The organic solutes were partitioned against aqueous HCl (ca. 6 N, 2 x 10 ml) and sat $NaHCO_3$ soln (10 ml), and dried (Na_2SO_4). Rota-evaporation then gave 230 mg (72%) of an oil which was submitted to flash chromatography on silica (70 g; column length 52, diameter 2 cm) with ether as eluent. The major fraction consisted of L-8 (200 mg, 62%) which solidified on storage in the refrigerator; m.p. 44-46°, $[\alpha]_D^{20}$ = +2.1°(c = 1.53, $CHCl_3$). IR (KBr): 3470 (b), 1590, 1350, 1210, 1170 cm^{-1}. ^1H, ^{13}C NMR see Tables 1,2. [Found: C, 52.32; H, 5.98. Calc for $C_{12}H_{16}O_5S$ (273.3): C, 52.92; H, 5.93%.]

(2R,3S)-2,3-O-Isopropylidene-1-O-p-tosyl-4-pentene-1,2,3-triol (L-9) from *erythro*-tosylate L-8: 70 mg (0.26 mmol) of L-8, 0.1 ml (0.78 mmol) of 2,2-dimethoxypropane, and $SnCl_2$ (catalytic amount) in dimethoxyethane (5 ml)

Table 1. ^{1}H NMR data of divinylcarbinol **1**, epoxypentenols **2**, **5**, pentenetriols **3**, **4** and derivatives **6**-**9**, **11**-**14**[a]

Compound	Chemical Shifts δ								
	1-H_c (1-H_a)	1-H_t (1-H_b)	2-H	3-H	4-H	5-H_E	5-H_Z	OH	Others
1	(see 4-H, 5-H_E, 5-H_Z)			4.62	5.89	5.15	5.27	2.25	
L-2 (erythro)	2.79	2.75	3.08	4.28	5.85	5.25	5.38	2.77 (b)	
L-3 (erythro)	3.37	3.37	3.48	3.88	5.95	5.05	5.19	4.38, 4.51, 4.75	
D-4 (threo)	3.24 - 3.39		3.46	3.97	5.89	5.04	5.21	4.43, 4.49, 4.62	
L-5 (threo)	3.66	3.92	3.08	3.39	5.61	5.31	5.49	3.29	
L-6 (erythro)	4.36	3.66	3.64	4.03	5.98	5.37	5.50	-	5.55 (6-H), 7.35 - 7.53 (C_6H_5)
L-7 (erythro)	3.92	3.59	3.72	4.15	5.94	5.23	5.46	-	1.06 [$C(CH_3)_3$], 5.49 (PhCH), 7.2 - 7.7 (3 C_6H_5)
L-8 (erythro)	4.08	4.12	3.88	4.22	5.83	5.23	5.31	2.81 (b), 3.15 (b)	2.46 ($ArCH_3$), 7.34 - 7.37, 7.78 - 7.81 (AA'BB' of C_6H_4)
L-9 (erythro)	3.89	4.00	4.33	4.64	5.71	5.22	5.38	-	1.33, 1.38 [$C(CH_3)_2$]; 2.44 ($ArCH_3$); 7.34 - 7.37, 7.78 - 7.81 (AA'BB' of C_6H_4)
L-11 (erythro)	3.90	3.98	4.07	4.22	5.87	5.23	5.38	3.62	1.36, 1.44 [$C(CH_3)_2$]
D-12 (threo)	3.75	3.97	4.05	4.21	5.80	5.24	5.37	3.62	1.37, 1.45 [$C(CH_3)_2$]
D-13 (threo)	-[b]	-[b]	-[b]	4.23	5.77	5.24	5.32	-[b]	2.48; -[b]
D-14 (threo)	4.07	4.18	3.85	4.27	5.78	5.24	5.32	-	1.35, 1.38 [$C(CH_3)_2$]; 2.44 ($ArCH_3$); 7.33 - 7.38, 7.78 - 7.81 (AA'BB' of C_6H_4)

Compound	Coupling Constants J									
	$J_{1c,t}$ ($J_{1a,1b}$)	$J_{1c,2}$ ($J_{1a,2}$)	$J_{1t,2}$ ($J_{1b,2}$)	$J_{2,3}$	$J_{3,4}$	$J_{3,5E}$	$J_{3,5Z}$	$J_{4,5E}$	$J_{4,5Z}$	$J_{5E,5Z}$
1	(see following values)				5.8	1.3	1.3	10.3	17.3	1.3
L-2	5.0	2.8	4.0	3.5	6.3	1.3	1.3	10.7	17.3	1.3
L-3	-[c]	-[c]	-[c]	5.5	5.5	1.8	1.8	10.5	17.5	1.8
D-4	-[c]	-[c]	-[c]	5.0	5.0	1.8	1.8	10.5	17.5	1.8
L-5	12.5	4.5	2.3	1.7	7.5	1.5	1.5	10.0	17.5	1.0
L-6	10.4	10.0	5.4	-[c]	7.0	0.8	1.3	10.5	17.0	1.4
L-7	10.4	10.3	4.9	9.8	6.1	-[d]	1.3	10.6	17.0	1.3
L-8	10.5	6.6	3.8	5.0	6.2	1.4	1.4	10.6	17.3	1.4
L-9	10.1	6.7	5.1	6.6	6.8	1.2	1.2	10.4	17.2	1.3
L-11	8.5	6.5	6.5	5.0	5.5	1.5	1.5	10.5	17.5	1.5
D-12	8.5	6.5	6.5	1.5	6.0	1.5	1.5	10.5	17.5	1.5
D-13	-[b]	-[b]	-[b]	8.5	7.0	0.9	0.9	10.0	17.5	1.0
D-14	11.0	5.0	3.7	7.8	7.0	0.9	0.9	10.2	17.0	1.0

Table 2. ^{13}C NMR data of divinylcarbinol **1**, epoxypentenols **2**, **5**, pentenetriols **3**, **4**, and derivatives **6** - **9**, **11** - **14** [a,b]

Compound	C-1	C-2	C-3	C-4	C-5	Others
1	115.3	139.3	73.9	139.3	115.3	-
L-**2**	43.7	54.0	70.5	135.8	117.4	-
L-**3**	63.0	72.7	74.7	139.5	114.3	-
D-**4**	62.5	72.1	74.4	139.2	114.2	-
L-**5**	61.4	56.0	60.3	134.9	119.8	-
L-**6**	70.8	65.2	83.3	134.6	118.1	100.9 (Ph-CH); 126.2, 128.2, 128.9, 137.7 (p-C_6H_4)
L-**7**	71.5	67.4	82.9	134.9	118.1	19.3, 26.9 [C(CH_3)$_3$], 100.5 (Ph-CH)[c]
L-**8**	70.8	72.0	73.1	135.6	117.89	21.6 (Ar-CH_3); 128.0, 129.9, 132.6, 145.1 (p-C_6H_4)
L-**9**	68.5	75.3	77.9	131.9	119.3	21.6 (Ar-CH_3); 25.3, 27.6, 109.5 [(H_3C)$_2$C]; 128.0, 129.8, 132.8, 144.9 (p-C_6H_4)
L-**11**	65.3	78.7	72.2	136.5	116.6	109.5 [$\underline{C}Me_2$]; 25.2, 26.5 [C$\underline{Me_2}$]
D-**12**	65.8	78.3	74.0	136.3	117.6	109.8 [$\underline{C}Me_2$]; 25.3, 26.7 [C$\underline{Me_2}$]
D-**13**	70.6	71.7	72.1	136.2	117.6	21.4 (Ar-CH_3); 127.8, 129.8, 132.6, 144.9 (p-C_6H_4)
D-**14**	68.1	78.1	78.8	134.5	119.3	21.5 (Ar-CH_3); 26.6, 26.9, 109.9 [(H_3C)$_2$C]; 127.9, 129.9, 132.9, 145.0 (p-C_6H_4)

[a] Recorded at 50.3 (**1**) and 100.6 MHz (others) in $CDCl_3$ except for L-**3**, D-**4** (in DMSO-d_6).
[b] Assignments for signals of same multiplicity with $\Delta\delta$ < 2 ppm may be reversed.
[c] 10 additional signals for the 3 C_6H_5 between 126.0 and 137.7 ppm.

Footnotes Table 1:

[a] Recorded at 200 (**1**) and 400 MHz (others) in $CDCl_3$ except for L-**3**, D-**4** (in DMSO-d_6).
[b] From 57 : 43 mixture of L-**8**/D-**13**; signals/couplings in part not identified.
[c] Not identified due to overlapping signals.
[d] Not observed.

were heated for 2 h to 60°. After cooling to room temp. one drop of pyridine was added and the mixture evaporated. The residue was recrystallized twice from ether/pentane (1:1) to give 50 mg (63%) of colourless needles; m.p. 55-56°, $[\alpha]_D^{20}$ = +42.5°(c = 0.57, $CHCl_3$). Authentic D-9 of >99.8% enantiomeric purity (from D-ribonolactone) showed m.p. 56-57°, $[\alpha]_D^{20}$ = -44.5°(c = 1.87, $CHCl_3$);[2a,12] this indicates a 97:3 enantiomer composition of the above sample of L-9. IR(KBr): 3090, 3060, 1600, 1365, 1175 cm^{-1}. ^1H, ^{13}C NMR see Tables 1,2; data in complete agreement with data of D-9.[12]

2,3-O-Isopropylidene-1-tosylate L-9 from (R)-glyceraldehyde acetonide (10)

(2R,3S)-1,2-O-Isopropylidene-4-pentene-1,2,3-triol L-11 (*erythro*) and (2R, 3R)-isomer (*threo*) D-12 from 10: Within 30 min glyceraldehyde acetonide 10 (6.30 g, 48.6 mmol, freshly prepared) was dropwise added to vinylmagnesium bromide in abs THF (93 ml of 1.04 M soln, 96.3 mmol) at room temp, and the mixture heated under reflux for 1 h. After cooling ether (25 ml) was added, followed by a sat soln of NH_4Cl (38 ml) at 0°. The precipitate was filtered and washed with ether (4 x 40 ml); the combined organic solutes were dried (K_2CO_3; Na_2SO_4). Rotaevaporation and distillation then gave a colourless oil; 6.23 g (81%), b.p. 80-85°/1 Torr, composition 60% L-11 and 40% D-12 (from ^1H NMR with addition of 6% Eu(fod)$_3$-d_{27} and integration of acetonide methyl absorptions; lit[23a] (preparation with vinylmagnesium chloride) : 65%, b.p. 41-42°/0.1 Torr, d.r. ca. 60 : 40 by GLC. IR (film): 3460 (b), 3080, 2980, 1375, 1365, 1245, 1205, 1060 cm^{-1}. ^1H, ^{13}C NMR, see Tables 1,2. NMR data of L-11 were in close agreement with those of D-11 prepared from D-ribonolactone D-15.[12]

(2R,3S)-4-Pentene-1,2,3-triol L-3 (*erythro*) and (2R,3R)-isomer D-4 (*threo*) from hydrolysis of acetonides L-11/D-12: The above 60:40 mixture of diastereomeric acetonides L-11/D-12 (1.90 g, 9.40 mmol) was treated with 15 ml of 2 N HCl in THF (15 ml) for 2 h at 60°. The resulting soln was cooled, neutralized with 2N NaOH (16 ml), and separated from the precipitate formed. After evaporation of solvents the remainders were distilled (Kugelrohr, 0.1 Torr) to afford a yellow liquid (1.04 g, 93%) which on redistillation gave a colourless oil; 0.95 g (85%), b.r. 120-160°/0.1 Torr; $[\alpha]_D^{18}$ = +1.1°(c = 2.6335, CH_3OH). GC purity on L/D-Chirasil-Val: L-3 62.1/62.48, D-4 37.7/37.43, D-3 and L-4 < 0.1/ < 0.1%. ^1H NMR (60 MHz) of this mixture showed chemical shift and coupling values for L-3 in close agreement to those of epoxidation product samples (cp. Tables 1,2); for the data of D-4, see Tables 1,2. With the value of >99.8% pure D-3 ($[\alpha]_D^{20}$ = +27.6°, from D-ribonolactone)[12] the estimate for the specific rotation of the *threo*-triol D-4 is ca +48°.

1-O-p-Tosyl-4-pentene-1,2,3-triols L-8 (*erythro*) and D-13 (*threo*) from the triols L-3/D-4: At 0° tosyl chloride (3.81 g, 20.0 mmol) was added to a 57:43 mixture of diastereomeric alcohols L-3/D-4 (2.30 g, 19.5 mmol) and pyridine (3.50 ml, 43.2 mmol) in CH_2Cl_2 (60 ml). The soln was kept at 0° for 24 h and then washed with aqueous HCl (0.1 N, 20 ml). The aqueous phase was extracted with CH_2Cl_2 (2 x 40 ml) and the combined organic layers were dried (Na_2SO_4) and evaporated to give 4.50 g (85%) of a yellow oil. After flash chromatography on silicagel (130 g; column 50 cm x 3 cm, eluent ether/ethyl acetate/triethylamine 8 : 2 : 0.1) 3.10 g (59%) of a colourless oil consisting of L-8/D-13 and 23% ethyl acetate (from ^1H NMR) was obtained; corrected yield of L-8/D-13 2.80 g (53%). ^1H, ^{13}C NMR data of L-8 in agreement with those of L-8 samples obtained via epoxidation; for ^1H, ^{13}C NMR data of these and D-13 see Tables 1,2.

(2R,3S)-2,3-O-Isopropylidene-1-O-p-tosyl-4-pentene-1,2,3-triol (L-9) and (2R,3R)-isomer D-14 from the tosylates L-8/D-13: 1.77 g of the mixture L-8/D-13 (containing 23% ethyl acetate; 1.60 g, 5.86 mmol pure L-8/D-13), 2,2-dimethoxypropane (1.20 ml, 10.0 mmol) and $SnCl_2$ (5 mg, 0.03 mmol) in dimethoxyethane (30 ml) were heated for 75 min to 80°. After cooling to room temp two drops of pyridine were added and the mixture was evaporated to give 1.80 g (98%) of a yellow oil. Flash chromatography on silica (130 g; column 50 cm x 3 cm), eluent ether/ethyl acetate/triethylamine 8 : 2 : 0.1 gave 0.90 g (63%) of colourless, spectroscopically pure oil. 330 mg of this oil was crystallized twice from petrol ether to give 116 mg (22%) of analytically pure crystals, which consisted of L-9/D-14 in a ratio of 92 : 8 (from ^1H NMR with addition of 40 mol-% Eu(fod)$_3$-d_{27} and integration of acetonide methyl absorptions); m.p. 51-52°; ^1H, ^{13}C NMR data, in agreement with those of L-9 obtained from the epoxidation, are listed in Tables 1,2. [Found: C, 57.83; H, 6.37. Calc for $C_{15}H_{20}O_5S$ (312.4): C, 57.67; H, 6.45%.]Evaporation of the filtrate (from the first crystallization) gave an oil (145 mg, 28%) that consisted of L-9/D-14 in a ratio of 24 : 76 (from ^1H NMR with addition of 35 mol-% Eu (fod)$_3$-d_{27} and integration as above). ^1H, ^{13}C NMR data of D-14 see Tables 1,2.

Acknowledgements - This work was supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Bayer AG, Wuppertal (Prof.H. Meyer). We also thank Degussa AG, Hanau, for gifts of chemicals, Mrs. E. Ruckdeschel and Dr. D. Scheutzow for recording the NMR spectra, and Ms. D. Michel, Ms. S. Schweizer (undergraduate research participant, spring 1986), Dipl.-Chem. W. Hümmer, Dipl.-Chem. R. Müller, and Dr. T. Gracza (A.v.Humboldt post-doctoral fellow 1987/8) for carrying out several experiments. We are particularly grateful to Dr. D. Wild, Institut für Pharmakologie und Toxikologie der Universität Würzburg, for establishing the toxicity and mutagenicity data of 1, L-2, and L-5. Finally, the help of Mrs. B. Jordan, Dipl.-Chem. U. Stahl and P. Poggendorf in the preparation of this paper are noted with gratitude.

REFERENCES

1. a) Part of the Dissertation of D. Schröter, Universität Würzburg, 1990. - b) The concept of this work was first presented at the Xth International Congress of Heterocyclic Chemistry, Waterloo/Canada, August 1985, see Ref. 8-10.
2. a) Preliminary communication: Häfele, B.; Schröter, D.; Jäger, V. *Angew. Chem.* **1986**, *98*, 89; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 87. - b) CGC analyses on chiral stationary phases: Koppenhoefer, B.; Walser, M.; Schröter, D.; Häfele, B.; Jäger, V. *Tetrahedron* **1987**, *43*, 2059.
3. Katsuki, T.; Sharpless, K.B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
4. Martin, V.S.; Woodard, S.S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K.B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.
5. For reviews see, f.e.: a) Sharpless, K.B.; Behrens, C.H.; Katsuki, T.; Lee, A.W.M.; Martin, V.S.; Takatani, M.; Viti, S.M.; Walker, F.J.; Woodard, S.S. *Pure Appl. Chem.* **1983**, *55*, 589. - b) Behrens, C.H.; Sharpless, K.B. *Aldrichim. Acta* **1983**, *16*, 67. - c) Seebach, D.; Weidmann, B.; Widler, L. *Modern Synthetic Methods* **1983**, *3*, 217. - d) Masamune, S.; Choy, W.; Petersen, J.S.; Sita, C.R. *Angew. Chem.* **1985**, *97*, 1; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1. - e) Pfenninger, A. *Synthesis* **1986**, 89. - f) Finn, M.G.; Sharpless, K.B., in Morrison, J.D. (ed), *Asymmetric Synthesis*, Vol. 5, p. 247 ff, Academic Press, New York 1985. - g) Rossiter, B.E. *ibid.*, p. 193 ff. - h) Schinzer, D. *Nachr. Chem. Tech. Lab.* **1989**, *37*, 1294.
6. For some recent examples see: a) Bernet, B.; Vasella, A. *Tetrahedron Lett.* **1983**, 5491; Julina, R.; Herzig, T.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1986**, *69*, 368. - b) Johnston, B.D.; Oehlschlager, A.C. *Can. J. Chem.* **1984**, *62*, 2148. - c) Adams, C.E.; Walker, F.J.; Sharpless, K.B. *J. Org. Chem.* **1985**, *50*, 420. - d) Roush, W.R.; Adam, M.A.; *J. Org. Chem.* **1985**, *50*, 3752. - e) Küfner, U.; Schmidt, R.R. *Angew. Chem.* **1986**, *98*, 90; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 89. - f) Overman, L.E.; Lin, N.-H. *J. Org. Chem.* **1985**, *50*, 3669. - g) Denis, J.-N.; Greene, A.E.; Serra, A.A.; Luche, M.-J. *J. Org. Chem.* **1986**, *51*, 46. - h) Gao, Y.; Hanson, R.M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. - i) Tamm, C.; Mohr, P. *Tetrahedron Lett.* **1987**,*28*, 391, 395. - j) Wershofen, S.; Scharf, H.-D. Scharf *Synthesis* **1988**, 854. - k) Schmidt, U; Respondek, M.; Lieberknecht, A; Werner, J.; Fischer, P. *Synthesis* **1989**, 56. - l) Schreiber, S.L.; Smith, D.B. *J. Org. Chem.* **1989**, *54*, 9. - m) Nicolaou, K.C.; Hwang, C.-K.; Duggan, M.E. *J. Am. Chem. Soc.* **1989**, *111*, 6682. - n) Kitagawa, I.; Shibuya, H.; Kawashima, K.; Ikeda, M. *Tetrahedron Lett.* **1989**, *30*, 7205. - o) Ernst, B.; Wagner, B.; *Helv. Chim. Acta* **1989**, *72*, 165. - p) Caldwell, C.G.; Bondy, S.S. *Synthesis* **1990**, 34.
7. Izumi, Y.; Tai, A. *Stereo-differentiating Reactions*, p. 64 f., Kodansha Ltd., Tokyo/Academic Press, New York-San Francisco-London 1977.
8. Jäger, V.; Müller, I.; Schohe, R.; Frey, M.; Ehrler, R.; Häfele, B.; Schröter, D. *Lect. Heterocycl. Chem.* 1985, *8*, 79.
9. Jäger, V.; Franz, R.; Schwab, W.; Häfele, B.; Schröter, D.; Schäfer, D.; Hümmer, W.; Guntrum, E.; Seidel, B., Proc. IXth SCHC, Bratislava/CSSR, August 23-28, 1987 in 'Studies in Organic Chemistry', Vol.35, *Chemistry of Heterocyclic Compounds*, Kovác, J.; Zálusky, P. (eds), pp 58-75, Elsevier, Amsterdam-Oxford-New York-Tokyo 1988.
10. a) The DVC epoxidation was independently conceived by Hatakeyama, S.; Sakurai, K.; Takano, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1759. - b) For a related concept using triene diols see : Hoye, T.R.; Suhadolnik, J.C. *J. Am. Chem. Soc.* 1985, *107*, 5312. - c) Epoxidation of DVC to yield racemic products: P. Chautemps, C. R. Acad. Sci. **1977**, *284*, 807 and ref.28 (Stoddart)
11. For applications and extensions of this concept see a) Hatakeyama, S.; Sakurai, K.; Takano, S. *Tetrahedron Lett.* **1986**, 4485. - b) Babine, R.E. *Tetrahedron Lett.* **1986**, 5791. - c) Schreiber, S.L.; Schreiber, T.S.; Smith, D.B. *J. Am. Chem. Soc.* **1987**, *109*, 1525. - d) Nicolaou, K.C.; Webber, S.E.; Ramphal, J.; Abe, Y. *Angew. Chem.* **1987**, *99*, 1077; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1019. - e) Okamoto, S., Kobayashi, Y., Kato, H.; Hori, K.; Takahashi, T.; Tsuji, J.; Sato, F. *J. Org. Chem.* **1988** , *53*, 5590. - f) Askin, D.; Volante, R.P.; Reamer, R.A.; Ryan, K.M.; Shinkai, I. *Tetrahedron Lett.* **1988**, *29*, 277. - g) Askin, D.; Volante, R.P.; Ryan, K.M.; Reamer, R.A.; Shinkai, I. *Tetrahedron Lett.* **1988**, *29*, 4245. - h) Nokami, J.; Ogawa, H.; Miyamoto, S.; Mandai, T.; Wakabayashi, S.; Tsuji, J. *Tetrahedron Lett.* **1988**, *29*, 5181. - i) Kobayashi, Y.; Kato, N.; Shimazaki, T.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 6297. - j) Synthesis of *erythro*-1- or -3-amino-4-pentenediols: Hümmer, W.; Gracza, T.; Jäger, V. *Tetrahedron Lett.* **1989**, *39*, 1517. - k) Synthesis of dihydroxy-pyrrolidines : Jäger, V.; Wehner, V.; Hümmer, W. et al. *22. GdCh-Hauptversammlung*, Bonn (1989), Abstr. OCH 3, p. 343; Jäger, V.; Hümmer, W. Angew. Chem. **1990**, *102*, 1182; Angew. Chem. Int. Ed. Engl. **1990**, *29*, 1171; Jäger, V.; Hümmer, W. Gracza, T.; Stahl, U.; paper to be submitted. - l) Morishima, H.; Kolke, Y.; Nakano, M.; Atsuumi, S.; Tanaka, S.; Matsuyama, K. *Eur. Pat. Appl.* 88114374.7 (1988), Banyu Pharmaceutical Co. Ltd.; we are grateful to Dr. H. Heitsch, Hoechst AG.
13. Miginiac, P. *Ann. Chim.* **1962**, 7, 445.

14. Hill, J.G.; Sharpless, K.B. *Org. Synth.* **1984**, *63*, 66.
15. Hanson, R.M.; Sharpless, K.B. *J. Org. Chem.* **1986**, *51*, 1922. We thank Prof. Sharpless for providing a preprint of this paper.
16. Klunder, J.M.; Koo, S.Y.; Sharpless, K.B. *J. Org. Chem.* **1986**, *51*, 3710; Ko ,S.Y.; Masamune, H.; Sharpless, K.B. *J. Org. Chem.* **1987**, *52*, 667.
17. Hümmer, W., *Dissertation* (planned 1991), Würzburg; similar results were achieved at Lederle, Pearl River/USA, by Dr. Babine and coworkers, cf. ref. 11b. We thank Dr. Babine for disclosing this and related informations.
18. Nakatsuka, M.; Ragan, J.A.; Sammakia, T.; Smith, D.B.; Uehling, D.E.; Schreiber, S.L. *J. Am. Chem. Soc.* **1990**, *112*, 5583; Smith, D.B.; Wang; Z.; Schreiber, S.L. *Tetrahedron* **1990**, *46*, 4793.
19. Lake, W.H.G.; Peat, S. *J. Chem. Soc.* **1939**, 1069; Newth, F.H. *Q. Rev. Chem. Soc.* **1959**, *13*, 30; Guthrie, R.D., in *The Carbohydrates*, Pigman, W.; Horton, D. (eds), 2nd ed., Vol. IA, pp. 468 f, Academic Press, New York 1972.
20. Payne, G.B. *J. Org. Chem.* **1962**, *27*, 3819.
21. See, e.g., studies cited in ref.5b; Wrobel, J.E.; Ganem, B. *J. Org. Chem.* **1983**, *48*, 3761.
22. *Synthesis* of L-5 from pentadienol: ref. 6j; cf. also: Sharpless, K.B. *Janssen Chim. Acta* **1988**, *6*, 3. - Racemic series: Holland, D.; Stoddart, J.F. *J.Chem. Soc. Perkin Trans I*, **1983**,1553.
23. a) Walton, D.J. *Can. J. Chem.* **1967**, *45*, 2921; cf. Horton, D.; Hughes, J.B. *J. Org. Chem.* **1968**, *33*, 728. - b) Mulzer, J.; Angermann, A. *Tetrahedron Lett.* **1983**, *24*, 2843. - For reviews see: Mulzer, J. *Nachr. Chem. Tech. Lab.* **1984**, *32*, 16; McGarvey, G.J.; Kimura, M.; Oh, T.; Williams, T.M. *J. Carbohydr. Chem.* **1984**, *3*, 125; Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447.
24. See footnote by Jäger, V.; Müller, I. *Tetrahedron* **1985**, *17*, 3519; cp. also recent catalogues of Fluka AG, Buchs, Switzerland.
25. Chen, C.-S.; Fujimoto, Y.; Sih, C.J. *J. Am. Chem. Soc.* **1981**, *103*, 3580; Chen, C.-S., Fujimoto, Y.; Girdaukas, G.; Sih, C.J. *J. Am. Chem. Soc.* **1982**, *104*, 7294; Wang, Y.-F.; Chen, C.-S.; Girdaukas, G.; Sih, C.J. *J. Am. Chem. Soc.* **1984**, *106*, 3695; Brooks, D.W.; Mazdiyasni, H.; Grothaus, G.G. *J. Org. Chem.* **1987**, *52*, 3223; Lam, L.K.P.; Brown, C.M.; DeJeso, B.; Lym, L.; Toone, E.J.; Jones, J.B. *J. Am. Chem. Soc.* **1988**, *110*, 4409; Gutman, A.L.; Bravdo, T. *J. Org. Chem.* **1989**, *54*, 4263.
26. For a review on other examples of diol oxidations, dione reductions, and di-ester hydrolyses see, f.e., Jones, J.B. *Tetrahedron* **1986**, *42*, 3351.
27. Mislow, K.; Berger, J.G. *J. Am. Chem. Soc.* **1962**, *84*, 1956; Brown, H.C.; Desai, M.C.; Jadhav, P.K. *J. Org. Chem.* **1982**, *47*, 5065; Partridge, J.J.; Chadha, N.K.; Uskokovic, M.R. *J. Am. Chem. Soc.* **1973**, *95*, 532, 7171; Whitesell, J.K.; Allen, D.E. *J. Org. Chem.* **1985**, *50*, 3025; cp. Whitesell, J.K. *Acc. Chem. Res.* **1985**, *18*, 280; Eder, U.; Sauer, G.; Wiechert, R. *Angew. Chem.* **1971**, *83*, 492; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 496; Hajos, Z.G.; Parrish, D.R. *J. Org. Chem.* **1974**, *39*, 1615; Ward, R.S. *Chem. Soc. Rev.* **1990**, *19*, 1.
28. Achiral substrates with enantio- and diastereotopic groups/faces opposed to achiral reagents, e.g.: Holland, D., Stoddart, J.F. *Carbohydr. Res.* **1982**, *100*, 207 (DVC); Oppolzer, W.; Burford, S.C.; Marazza, F. *Helv. Chim. Acta* **1980**, *63*, 555 and papers cited (O-silyl DVC); cp. Ley, S.V.; Sternfeld, F.; Taylor, S. *Tetrahedron Lett.* **1987**, *28*, 225.
29. See, for example: Eliel, E.L. *Topics Curr. Chem.* **1982**, *105*, 1; Hirschmann, H.; Hanson, H. Topics Stereochem. **1983**, *14*, 183; Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319.
30. Cp. also: Cahn, R.S.; Ingold, C.K.; Prelog, V. *Angew. Chem.* **1966**, *78*, 413; Prelog, V.; Helmchen, G. *Helv. Chim. Acta* **1972**, *55*, 2581; id., *Angew. Chem.* **1982**, *94*, 614; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 567; Seebach, D.; Prelog, V. *Angew. Chem.* **1982**, *94*, 696; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 654.
31. Hanson, K.R.; Rose, I.A. *Acc. Chem. Res.* **1975**, *8*, 1.
32. For correspondence concerning these studies please address to: Dr. D. Wild; Institut für Pharmakologie und Toxikologie der Universität, Versbacher Str.9, D-8700 Würzburg/FRG.
33. Simon, P.; Epe, B.; Mutzel, P.; Schiffmann, D.; Wild, D.; Ottenwälder, H.; Fedtke, N.; Bolt, H.M.; Henschler, D. *J. Biochem. Toxicol.* **1986**, *1*, 43.
34. Toxicology department, BASF AG, Ludwigshafen. We thank Dr. P. Thieme, Dr. V. Schulz and Prof. Dr. U. Schenk for this information.
35. Dumont, R.; Pfander, H. *Helv. Chim. Acta.* **1983**, *66*, 814.
36. Häfele, B.; Jäger, V. *Liebigs Ann. Chem.* **1987**, 85.