146. The Reaction of 1,2:3,4-Diepoxy-2,3-dimethylbutane with Nucleophiles[1])

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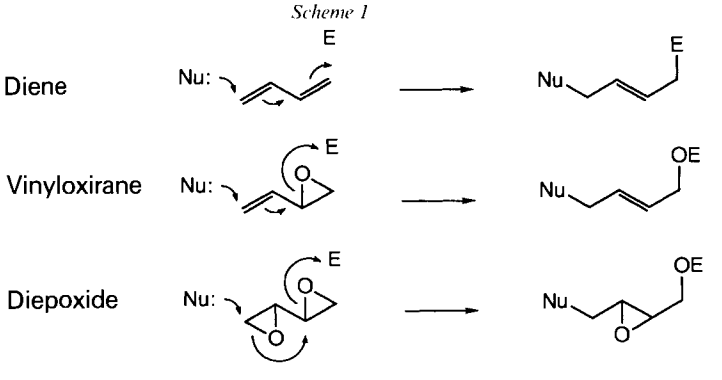
To find out whether the 1,4-addition to 1,2:3,4-diepoxides, which so far has been observed only once, is of a more general character, we investigated the reaction of a variety of O-, C-, N-, and S-nucleophiles with the model compound 1,2:3,4-diepoxy-2,3-dimethylbutane (*Scheme 4*). In several cases, 1,4-addition products could, indeed, be observed besides the expected 1,2-adducts (*Table*).

The 1,4-addition to conjugated dienes is a well known reaction (*cf. Sweeting* and *Johnson* [4]). Similarly, vinyloxiranes can react as an entity: a nucleophile can attack the double bond, which is subsequently shifted by simultaneous opening of the epoxide (*cf. e.g.* [5]). One could imagine that 1,2:3,4-diepoxides might undergo an analogous 1,4-addition with migration of the epoxide as pointed out in *Scheme 1*.

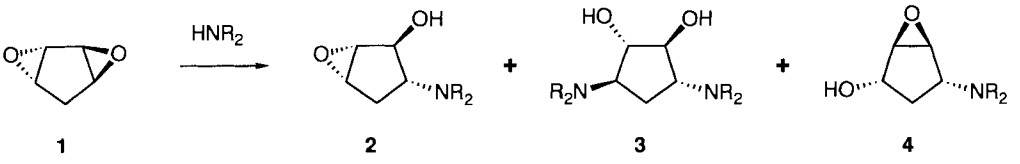
Scheme 1



The reaction of 1,2:3,4-diepoxides towards nucleophiles has so far been investigated only in a few cases (see, *e.g.*, [6–8] and additional refs. in [3]). Independent reaction of the two epoxide moieties was usually found. In contrast to this, *Kozlov et al.* [9] reported some years ago that *trans*-1,2:3,4-diepoxycyclopentane (**1**) reacted with secondary amines to give a product **4** with a central epoxy group which obviously arose from a 1,4-addition (*Scheme 2*). Besides **4**, the expected 1,2-addition products **2** and **3** were observed. In *trans*-1,2:3,4-diepoxycyclopentane (**1**), the two epoxy groups are held more

[1]) Presented in part by *F. F.* at the meeting of the Swiss Chemical Society, Bern, October 19, 1990. From the dissertation of *F. F.* [1], the diploma thesis of *Th. W.* [2], and the dissertation of *Th. E.* [3].

Scheme 2

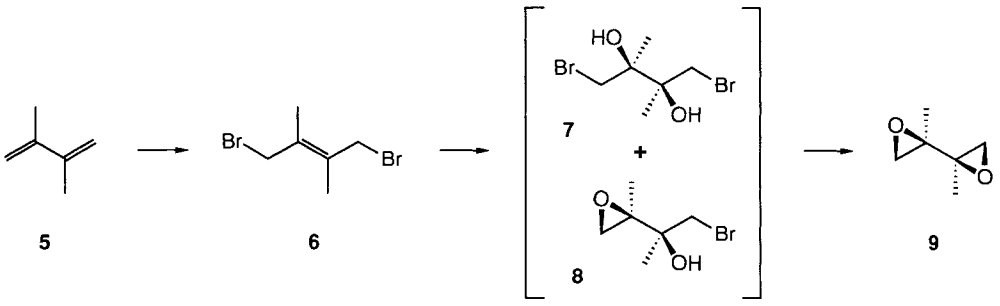


1 2 3 4

or less rigidly in an arrangement which should favor 1,4-addition. In contrast, in a compound where the two epoxy groups are not attached to a ring system, there is free rotation around the inter-epoxide bond, and the question arises, whether in such an 'open-chain diepoxide', a 1,4-addition could still be observed. We chose the racemic 1,2:3,4-diepoxy-2,3-dimethylbutane (**9**) as the model compound for the investigation of this problem. The methyl groups at C(2) and C(3) of **9** will guide the nucleophile to attack regioselectively the sterically less hindered atoms C(1) and C(2) and thus limit the number of products.

Direct epoxidation of 2,3-dimethylbuta-1,3-diene (**5**) yields both diastereoisomers of the corresponding diepoxide [10]. It was, however, not possible to separate them. On the other hand, racemic **9** is easily accessible by a short stereoselective synthesis. Thus, in analogy to work by *Heasley* and coworkers [11], diene **5** was treated with Br_2 to give (*E*)-dibromide **6**, which was then converted with $KMnO_4$ and NaOH in a two-phase system to diepoxide **9** (*Scheme 3*); isolation of the intermediate bromohydrins **7** or **8** was not necessary. Confirmation of the configuration of **9** was given by a ^{1}H-NMR spectrum recorded in the presence of the chiral shift reagent [Eu(hfc)$_3$] which showed separate signals for all protons of the two enantiomers.

Scheme 3



5 6 7 + 8 9

Reaction of diepoxide **9** with nucleophiles should give rise to three general types of products, *i.e.* the regular 1,2-addition product **10**, the product **11** of a the twofold 1,2-addition, and the 1,4-addition product **12** (*Scheme 4*). The nucleophiles used and the products obtained are summarized in the *Table*. The product mixtures were first analyzed by GC and GC/MS, then the components were isolated and their structures determined spectroscopically. Most of the yields given in the *Table* are isolated yields; the balance to 100% consisted of unreacted starting material, unidentified decomposition products, and mixtures of the identified products that could not be separated.

Scheme 4

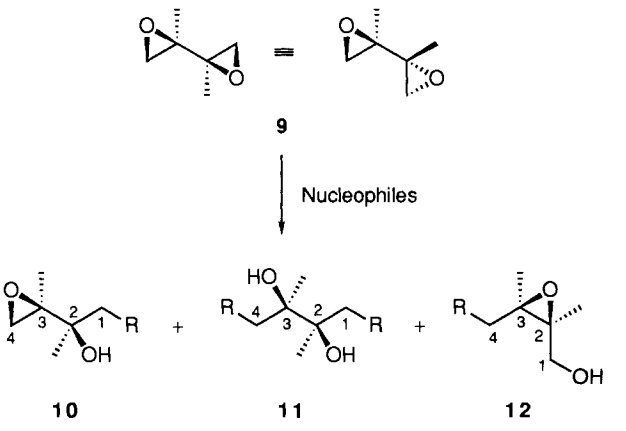


Table. *Products Isolated from the Reaction of Diepoxide* **9** *with Various Nucleophiles*

Nucleophile	Solvent	Reaction conditions	Products (Yields in %)			
			Type **10**	Type **11**	Type **12**	R
NaOMe (1.3 equiv.)	MeOH	24 h, r.t.	**10a** (52)[a])	**11a** (14)[a])	**12a** (31)[a])	MeO
$MeCu(CN)Li_2$ (1.1 equiv.)	Et_2O	10 h, −78°; 1 h, r.t.	**10b** (10)	**11b** (17)		Me
Et_2NH (1.0 equiv.)	MeOH	16 h, 50°			**12c** (20)[b])	Et_2N
Et_2NH (1.0 equiv.)	H_2O	17 h, 45°			**12c** (37)[a])	Et_2N
Piperidine (3.1 equiv.)	piperidine	28 h, 40°		**11d** (7)		Piperidin-1-yl
Morpholine (2.3 equiv.)	THF	24 h, r.t.; 48 h, 60°		**11e** (7)	**12e** (10)	Morpholin-4-yl
NaN_3 (4.5 equiv.)	acetone/H_2O	10 h, −22°; 10 h, r.t.	**10f** (16)	**11f** (1)	**12f** (26)	N_3
NaSPh (2.0 equiv.)	PhSH/H_2O	1.5 h, 0°	**10g** (17)	**11g** (20)		PhS
NaS(*t*-Bu) (1.0 equiv.)	*t*-BuSH/H_2O	0.3 h, 0°	**10h** (67)	**11h** (24)		*t*-BuS

[a]) Yields determined by GC.
[b]) Moreover, **11a** (5%) and **12a** (17%), formed by reaction with the solvent MeOH, were isolated.

Thus, reaction of diepoxide **9** with a slight excess of NaOMe yielded a mixture consisting mainly of **10a**/**11a**/**12a** which were very difficult to separate by column chromatography. When **9** was allowed to react with simple cuprates in THF, no products were formed. Since *Lipshutz* [12] noted a solvent effect for the reaction of higher-order cyanocuprates with epoxides, we tried the reaction in Et_2O and obtained the 1,2-adducts **10b**/**11b**; an additional isomer of **10b** was present in the product mixture according to GC/MS which might well be the corresponding 1,4-addition product **12b**. It could, however, not be isolated, since the chromatographic separation of the products proved to be very difficult.

Compound **9** would not give any products with Et_2NH under weakly polar aprotic conditions, even not after heating to 60° for 4 d. Addition occurred, however, in protic solvents. This is in accord with *Goldfarb*'s observation in 1941 that propylene oxide and Et_2NH did not react with each other; only upon addition of catalytic amounts of MeOH, a vigorous, exothermic reaction to 1-(diethylamino)propan-2-ol was observed [13]. The

product mixture that we obtained from the reaction of **9** with Et_2NH in MeOH consisted of 1,4-adduct **12c** as well as of the two compounds **11a** and **12a**, which stem from the reaction of **9** with the solvent. When H_2O was used as solvent in an attempt to optimize the yield of **12c**, the latter could be obtained in 37% yield.

Equimolar amounts of **9** and piperidine did not give any products, but use of an excess of piperidine without any further solvent at elevated temperature produced bis-adduct **11d** in 7% yield as the only product. For the reaction of **9** with morpholine, the temperature and the reaction time had to be increased further, and since in the reaction with piperidine only the bis-adduct was obtained, THF was used as cosolvent. Under these conditions, bis-adduct **11e** and 1,4-addition product **12e** were obtained in modest yields.

The reaction with NaN_3, which had to be carried out in acetone/H_2O 1:1 to get a homogeneous solution, led to the mixture **10f**/**11f**/**12f**, the 1,4-adduct **12f** being the main product. When the S-nucleophiles sodium thiophenolate or sodium *tert*-butyl sulfide were used, much milder reaction conditions could be used (→ **10g**/**11g** and **10h**/**11h**, resp.); however, no 1,4-adducts were obtained.

Our investigations show clearly that 'open-chain diepoxides' such as model compound **9**, indeed, do give 1,4-addition products in a similar way as was observed by *Kozlov et al.* for diepoxycyclopentane **1**. So far, our results do not allow to predict which nucleophiles will give this type of addition products nor which reaction conditions would favor their formation. No attempt was made to elucidate the mechanism leading to the 1,4-adducts **12**. So we do not know, whether it is a concerted reaction or whether a 1,2-addition is followed by a *Payne* rearrangement [14].

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Experimental Part

General. Reactions sensitive to air or H_2O were carried out under Ar. THF was freshly distilled over Na-K alloy; CH_2Cl_2 was distilled through a 80-cm column and stored over molecular sieves (4 Å); Et_2O was distilled over $FeSO_4$ and dried by storage over Na. All other reagents were of reagent grade and used without further purification. Org. extracts were dried (Na_2SO_4 or $MgSO_4$) and evaporated below 50°. TLC: silica gel *60* F_{254} (*Merck*). Column chromatography (CC): silica gel (60–200 μm or 35–70 μm, *Chemische Fabrik Uetikon*). M.p.: *Kofler* hot stage; corrected. IR: *Perkin-Elmer-781* IR spectrometer. NMR (*K. Aegerter, K. Ulrich, S. Peterli, M. Nikles*): *Varian EM 360* (^{1}H, 60 MHz), *Bruker WH 90* (^{1}H, 90 MHz; ^{13}C, 22.63 MHz), *Varian Gemini-300* (^{1}H, 300 MHz; ^{13}C, 75 MHz), and *Varian VXR-400* (^{1}H, 400 MHz; ^{13}C, 101 MHz); multiplicities in ^{13}C-NMR spectra, where listed, were determined by off-resonance decoupling, otherwise APT experiments were performed; chemical shifts in ppm rel. to internal TMS; * means that assignments may be interchanged. MS (Dr. *H. Nadig*): *VG-70-250* spectrometer. GC/MS: *Hewlett Packard 5790 A*/*5970 A*.

(E)-1,4-Dibromo-2,3-dimethylbut-2-ene (**6**). To a soln. of 73.03 g (0.889 mol) of 2,3-dimethylbuta-1,3-diene (**5**; *Fluka*) in 900 ml of CH_2Cl_2 at −78° and under Ar, 140.62 g (0.88 mmol) of Br_2 in 650 ml of CH_2Cl_2 were added slowly under stirring. After 5 h, the reaction was quenched by adding sat. $NaHCO_3$ soln. The org. layer was washed 3 times with cold H_2O, dried, and evaporated: crude green liquid which crystallized spontaneously in the cold. *Caution:* These operations must be carried out in a well ventilated hood since the crude product contains a tear-gas (probably bromoacetone). The crystals were dissolved in pentane, subjected to a short CC (pentane), and then recrystallized 2 times from pentane: 143.5 g (67%) of **6**. Colorless needles. M.p. 44.5–46° ([15]: 43–44°). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.00 (*s*, CH_2(1), CH_2(4)); 1,88 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 131.9 (C(2), C(3)); 35.0 (C(1), C(4)); 17.2 (CH_3–C(2), CH_3–C(3)).

The first few CC fractions contained a small amount of 1,2,3,4-tetrabromo-2,3-dimethylbutane [15] [16].

(2RS,3RS)-1,2:3,4-Diepoxy-2,3-dimethylbutane (**9**). A soln. of 125.5 g (0.52 mol) of **6** in 500 ml of CH_2Cl_2, 500 ml of 30% aq. NaOH soln. (2.1 mol), and 5.01 g of $(BnEt_3N)Cl$ were stirred at 0°. Then, 131.14 g (0.83 mol) of freshly pulverized $KMnO_4$ were added in small portions within 7 d. The dark brown, very viscous slurry was diluted with Et_2O at r.t. and stirred mechanically in order to break up the solid lumps that had formed. The org. layer was then separated and the sticky aq. residue washed several times with Et_2O. The combined org. soln. was filtered through *Celite* and dried, the solvent removed by distillation through a 35-cm *Raschig* column, and crude **9** distilled at 49°/20 mbar through a small column filled with metallic *Raschig* rings: 41.92 g (71%) of **9**. Colorless oil. IR (film): 3060, 2990, 2930, 1445, 1380, 1170, 1110, 1085, 1060, 1000, 895, 885, 850. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.82 (*d*, *J* = 5, 2 H, H–C(1), H–C(4)); 2,59 (*d*, *J* = 5, 1 H, H–C(1), H–C(4)); 1.39 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 56.4 (C(2), C(3)); 51.5 (C(1), C(4)); 18.4 (CH_3–C(2), CH_3–C(3)). CI-MS (NH_3): 132 (26, $[M + NH_4]^+$), 115 (100, $[M + 1]^+$), 97 (9), 69 (65), 58 (16).

(2RS,3RS)-1,4-Dibromo-2,3-dimethylbutane-2,3-diol (**7**) *and (2RS,3SR)-1-Bromo-3,4-epoxy-2,3-dimethylbutan-2-ol* (**8**). To a soln. of 4.80 g (20 mmol) of **6** in 20 ml of acetone under Ar was added a soln. of 3.20 g (20 mmol) of $KMnO_4$ in 100 ml of H_2O within 1 h. The mixture was stirred for 2 h at 0°, then for 1 h at r.t. and was finally filtered through *Celite*. The filtrate was extracted twice with 50 ml of CH_2Cl_2, the combined org. extract dried (Na_2SO_4) and evaporated, and the oily residue (1.83 g) consisting of **7**/**8**/**9** (20:49:2) subjected to fractional distillation at 13 mbar: at 30–88°, 256.8 mg of **8**/**9** (5:9); at 88–94°, 516.6 mg of **8**; at 94°, 30.3 mg of **8**; residue, 450.8 mg of **7**/**8** (41:6). The residue of the distillation was recrystallized from pentane: 338 (6.2%) of **7** [17] as colorless crystals. Alcohol **8** (547 mg) was purified by CC (30 g of SiO_2, CH_2Cl_2 with 0.75% of MeOH): 402 mg (10.4%) of **8** as colorless oil.

Data of **7**: M.p. 93–94.5° ([17]: 99°). IR (KBr): 3480, 3380 (br., OH), 2980, 1385, 1255, 1210, 1130, 1035, 955. ^{1}H-NMR (60 MHz, $CDCl_3$): 3.92 (*d*, *J* = 11, 2 H, H–C(1), H–C(4)); 3.58 (*d*, *J* = 11, 2 H, H–C(1), H–C(4)); 2.58 (*s*, 2 OH); 1.36 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 75.1 (*s*, C(2), C(3)); 45.4 (*t*, C(1), C(4)); 26.0 (*q*, CH_3–C(2), CH_3–C(3)). EI-MS: 183, 181 (15, 16, $[M - CH_2Br]^+$); 165, 163 (10, 10); 139, 137 (32, 34); 123, 121 (5, 5); 58 (100); 43 (99). CI-MS (NH_3): 296, 294, 292 (49, 100, 51, $[M + NH_4]^+$); 214, 212 (31, 31); 132 (4); 56 (11).

Data of **8**: IR (film): 3460 (br., OH), 3060, 2980, 2940, 1450, 1420, 1390, 1370, 1360, 1340, 1240, 1190, 1100, 1050, 1000, 940, 870, 840, 780. ^{1}H-NMR (90 MHz, $CDCl_3$): 3.64 (*d*, *J* = 10, 1 H, H–C(1)); 3.50 (*d*, *J* = 10, 1 H, H–C(1)); 2.90 (*d*, *J* = 5, 1 H, H–C(4)); 2.76 (*s*, OH); 2.48 (*d*, *J* = 5, 1 H, H–C(4)); 1.43, 1.37 (2*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 70.6 (*s*, C(2)); 60.2 (*s*, C(3)); 49.5 (*t*, C(4)); 41.1 (*t*, C(1)); 23.1 (*q*, CH_3–C(2)); 17.5 (*q*, CH_3–C(2)). EI-MS: 197, 195 (0.1, 0.1, $[M + 1]^+$); 139, 137 (5, 5); 101 (7); 85 (14); 69 (6); 58 (44); 57 (26); 43 (100). CI-MS (NH_3): 197, 195 (51, 52, $[M + 1]^+$); 179, 177 (97, 100, $[M - OH]^+$); 139, 137 (15, 18); 101 (18); 97 (45); 85 (84); 69 (90); 57 (35); 49 (18); 43 (97).

(2RS,3RS)-3,4-Epoxy-1-methoxy-2,3-dimethylbutan-2-ol (**10a**), *(2RS,3RS)-1,4-Dimethoxy-2,3-dimethylbutane-2,3-diol* (**11a**), *and (2RS,3SR)-2,3-Epoxy-4-methoxy-2,3-dimethylbutan-1-ol* (**12a**). To a soln. of 0.833 g (7.3 mmol) of **9** in 3 ml of MeOH, 4.7 ml (9.49 mmol) of 2.02M NaOMe in MeOH were added at r.t. and under anh. condition. The mixture was stirred for 1 d, diluted with 20 ml of Et_2O and quenched with 7 ml of H_2O. The H_2O phase was extracted 8 times with 10 ml of Et_2O, the combined org. phase dried and evaporated under mild vacuum, and the residue (GC: **9** (2%), **10a** (52%), **11a** (14%), **12a** (31%)) subjected to CC (300 g of silica gel, ∅ 8 cm, pentane/Et_2O 1:2): 41 mg (4%) of **10a** as a pure, colorless oil and 480 mg of **11a**/**12a**. For separation and data of **11a** and **12a**, see below.

Data of **10a**: IR (film): 3470 (br., OH), 2970, 2920, 2880, 1450, 1375, 1190, 1140, 1105, 1065, 970, 895, 855. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.53 (*d*, *J* = 9.5, 1 H, H–C(1)); 3.40 (*s*, MeO); 3.30 (*d*, *J* = 9.5, 1 H, H–C(1)); 2.91 (*d*, *J* = 5.2, 1 H, H–C(4)); 2.7 (br., OH, exchangeable with D_2O); 2.44 (*d*, *J* = 5.2, 1 H, H–C(4)); 1.37 (*s*, CH_3–C(3)); 1.20 (*s*, CH_3–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 77.7 (C(1)); 71.1 (C(2)); 60.1 (C(3)); 59.5 (CH_3O); 49.8 (C(4)); 21.2 (CH_3–C(2)); 17.9 (CH_3–C(3)). CI-MS (NH_3): 165 (8, $[M + 1 + NH_4]^+$), 164 (100, $[M + NH_4]^+$), 147 (25, $[M + 1]^+$), 146 (7), 134 (13), 132 (13), 129 (61, $[M - OH]^+$), 115 (14, $[M - MeO]^+$), 114 (13), 113 (32), 106 (13), 97 (22). EI-MS: 101 (13, $[M - CH_2OCH_3]^+$), 89 (12), 69 (11), 57 (14), 45 (31), 43 (100), 41 (12).

(2RS,3RS)-1,2-Epoxy-2,3-dimethylpentan-3-ol (**10b**), *and (3RS,4RS)-3,4-Dimethylhexane-3,4-diol* (**11b**). To a suspension of 0.786 g (8.7 mmol) of CuCN in 2 ml of abs. Et_2O were added 11 ml (17.6 mmol) of 1.6M MeLi in Et_2O (*Fluka*) at −78°. Subsequent warming to 0° for *ca.* 3 min led to a clear yellow soln., which was recooled immediately to −78°, followed by dropwise addition of 0.906 g (7.95 mmol) of **9** in 4 ml of abs. Et_2O. The mixture was stirred at −78° for 10 h, allowed to warm up to r.t., and quenched by adding 10 ml of sat. NH_4Cl/NH_4OH soln. (pH *ca.* 10). Then, the org. phase was washed twice with H_2O, dried, and evaporated. The residue (0.9 g of a clear viscous oil) was subjected to CC (100 g of silica gel, pentane/Et_2O 2:1): 98 mg (10%) of **10b** as a pure, colorless oil

and a second product. The latter was purified by further CC (80 g silica gel, pentane/BuOH 19:1): 199 mg (17%) of **11b** as a clear, colorless oil, which crystallized spontaneously in the cold and was recrystallized from pentane.

Data of **10b**: IR (film): 3485 (br., OH), 2980, 2940, 1460, 1390, 1160, 1120, 1075, 925, 850, 840. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.94 (*dq*, *J* = 5, 0.6, 1 H, H–C(1)); 2.46 (*d*, *J* = 5, 1 H, H–C(1)); 2.03 (br. *s*, OH); 1.73–1.56 (*m*, CH_2(4)); 1.35 (*d*, *J* = 0.6, CH_3–C(2)); 1.20 (*s*, CH_3–C(3)); 0.96 (*t*, *J* = 7.5, CH_3(5)). ^{13}C-NMR (101 MHz, $CDCl_3$): 71.4 (C(3)); 61.7 (C(2)); 50.1 (C(1)); 31.4 (C(4)); 23.4 (CH_3–C(3)); 17.9 (CH_3–C(2)); 7.5 (C(5)). CI-MS (NH_3): 149 (12, $[M + 1 + NH_4]^+$), 148 (100, $[M + NH_4]^+$), 131 (53, $[M + 1]^+$), 113 (59).

Data of **11b**: M.p. 52.6–53.4°. IR (KBr): 3400 (br., OH), 2985, 2940, 2880, 1470, 1380, 1360, 1270, 1180, 1140, 1125, 1110, 1045, 995, 925, 910. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.0 (*s*, 2 OH); 1.67 (*dq*, *J* = 14.3, 7.4, 2 H, H–C(2), H–C(5)); 1.43 (*dq*, *J* = 14.3, 7.4, 2 H, H–C(2), H–C(5)); 1.12 (*s*, CH_3–C(3), CH_3–C(4)); 0.96 (*t*, *J* = 7.4, CH_3(1), CH_3(6)). ^{13}C-NMR (101 MHz, $CDCl_3$): 77.2 (C(3), C(4)); 28.5 (C(2), C(5)); 20.0 (CH_3–C(3), CH_3–C(4)); 8.0 (C(1), C(6)). CI-MS (NH_3): 165 (5, $[M + 1 + NH_4]^+$), 164 (63, $[M + NH_4]^+$), 146 (14), 129 (100), 128 (17), 111 (91).

*(2*RS*,3*SR*)-4-(Diethylamino)-2,3-epoxy-2,3-dimethylbutan-1-ol* (**12c**), **11a**, *and* **12a**. To a soln. of 0.496 g (4.34 mmol) of **9** in 0.7 ml of MeOH, 0.3 ml (4.37 mmol) of Et_2NH were added at 0°. The mixture was stirred overnight at 50°, cooled to r.t., and evaporated. The residue was subjected to flash-CC (*RP-8-Lobar*, column size *B*, *Merck*; gradient H_2O/MeOH 5:1 → 1:10 then MeOH). The fractions were pooled to give 3 portions, each of which was continuously extracted with Et_2O. The extracts were dried and evaporated to yield pure, colorless oils: 104 mg (17%) of **12a**, 40 mg (5%) of **11a**, and 160 mg (20%) of **12c**.

Data of **12c**: IR (film): 3440 (br., OH), 2970, 2930, 2875, 2820, 1455, 1385, 1100, 1080, 1040, 855. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.74 (*d*, *J* = 11.8, 1 H, H–C(1)); 3.48 (*d*, *J* = 11.8, 1 H, H–C(1)); 2.85 (*d*, *J* = 13.3, 1 H, H–C(4)); 2.73 (*d*, *J* = 13.3, 1 H, H–C(4)); 2.71 (*dq*, *J* = 13.2, 7.3, 2 H, $(CH_3CH_2)_2N$); 2.44 (*dq*, *J* = 13.3, 7.3, 2 H, $(CH_3CH_2)_2N$); 1.77 (br. *s*, OH); 1.44, 1.46 (2*s*, CH_3–C(2), CH_3–C(3)); 1.05 (*t*, *J* = 7.2, $(CH_3CH_2)_2N$). ^{13}C-NMR (75 MHz, $CDCl_3$): 67.6 (C(1)); 65.4, 63.9 (C(2), C(3)); 59.9 (C(4)); 47.1 ($(CH_3CH_2)_2N$); 22.2 (CH_3–C(3)); 17.4 (CH_3–C(2)); 10.6 ($(CH_3CH_2)_2N$). CI-MS (NH_3): 189 (11, $[M + 2]^+$), 188 (100, $[M + 1]^+$), 130 (7), 86 (34). EI-MS: 130 (5), 114 (2), 98 (4), 87 (6), 86 (100), 58 (20).

Data of **11a**: IR (film): 3470 (br., OH), 2980, 2930, 2890, 2815, 1450, 1385, 1195, 1100, 970. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.63 (br., 2 OH, exchangeable with D_2O); 3.49 (*d*, *J* = 9.5, 2 H, H–C(1), H–C(4)); 3.43 (*d*, *J* = 9.5, 2 H, H–C(1), H–C(4)); 3.40 (*s*, 2 MeO); 1.20 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 79.1 (C(1), C(4)); 75.3 (C(2), C(3)); 59.7 (2 MeO); 20.9 (CH_3–C(2), CH_3–C(3)). CI-MS (NH_3). 196 (12, $[M + NH_4]^+$), 180 (9), 179 (100, $[M + 1]^+$), 161 (25, $[M - OH]^+$), 143 (12), 129 (11), 113 (7), 89 (5), 73 (81), 58 (18). EI-MS: 133 (17), 115 (11), 89 (55), 73 (10), 58 (32), 57 (28), 45 (37), 43 (100).

Data of **12a**: IR (film): 3440 (br., OH), 2980, 2930, 2820, 1455, 1380, 1190, 1105, 1035, 955, 855. ^{1}H-NMR (300 MHz, $CDCl_3$; with ^{1}H,^{1}H-decoupling experiments): 3.71 (br. *d*, *J* = 11.6, 1 H, H–C(1)); 3.61 (*d*, *J* = 11.6, 1 H, H–C(1)); 3.56 (*s*, CH_2(4)); 3.40 (*s*, MeO); 2.53 (br. *s*, OH); 1.44, 1.45 (2*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 77.1 (*t*, C(4)); 6.66 (*t*, C(1)); 64.6, 63.3 (2*s*, C(3), C(2)); 59.6 (*q*, MeO); 17.1, 17.9 (2*q*, CH_3–C(2), CH_3–C(3)). ^{1}H,^{13}C-COSY (400/101 MHz, $CDCl_3$): cross-peaks at δ(H), δ(C) 1.45, 17.1 (CH_3–C); 1.44, 17.9 (CH_3–C); 3.40, 59.6 (MeO); 3.61, 3.71, 66.6 (CH_2(1)); 3.56, 77.1 (CH_2(4)). CI-MS (NH_3): 165 (4, $[M + 1 + NH_4]^+$), 164 (59, $[M + NH_4]^+$), 147 (28, $[M + 1]^+$), 146 (9), 132 (9), 130 (9), 129 (100, $[M - OH]^+$), 115 (37, $[M - MeO]^+$), 114 (14), 113 (10), 106 (10), 101 (9), 98 (5), 97 (76), 73 (65), 58 (12). EI-MS: 115 (7, $[M - MeO]^+$), 101 (4), 89 (78), 75 (6), 73 (9), 71 (22), 58 (11), 57 (57), 45 (46), 43 (100), 41 (27), 39 (21).

*(2*RS*,3*SR*)-4-(Diethylamino)-2,3-epoxy-2,3-dimethylbutan-1-ol* (**12c**). A soln. of 0.800 g (7.01 mmol) of **9**, 7 ml of H_2O, and 0.357 g (7.3 mmol) of Et_2NH was stirred for 17 h at 45°. The soln. was then continuously extracted with Et_2O and the extract dried and evaporated. Of the crude product thus obtained, 37% proved to be identical to **12c** according to GC, TLC, and NMR.

*(2*RS*,3*RS*)-2,3-Dimethyl-1,4-di(piperidin-1-yl)butane-2,3-diol* (**11d**). A soln. of 87.4 mg (0.766 mmol) of **9** and 136 µl (1.38 mmol) of piperidine was warmed to 40° and stirred for 28 h. The soln. was evaporated and the residue subjected to CC (4 g of silica gel, pentane/Et_2O 10:1, then pentane/MeOH 20:1): 15.5 mg (7%) of **11d**. Colorless crystals. M.p. *ca.* 170° (dec.). IR (KBr): 3400 (br., OH), 2930, 1595, 1375, 1150, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.2 (br. *s*, 2 OH, exchangeable with D_2O)[2]); 2.92 (br. *s*, 4 H, 2 H–C(2′), 2 H–C(6′))[2]); 2.54 (*d*, *J* = 14, 2 H, H–C(1), H–C(4)); 2.40 (*d*, *J* = 14, 2 H, H–C(1), H–C(4)); 2.4 (br. *s*, 4 H, 2 H–C(2′), 2 H–C(6′))[2]); 1.57* (*quint.*, *J* = 5.5, 2 CH_2(3′), 2 CH_2(5′))[2]); 1.40* (br. *s*, 2 CH_2(4′))[2]); 1.06 (*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (300 MHz, CD_3OD): 2.92 (br. *s*, 4 H, 2 H–C(2′), 2 H–C(6′)); 2.67 (*d*, *J* = 14.4, 2 H, H–C(1), H–C(4)); 2.39 (*d*,

[2]) When the spectrum is recorded at 50°, these signals get sharper and taller; furthermore, the OH resonance is shifted to 4.39 ppm.

J = 14.4, 2 H, H–C(1), H–C(4)); 2.4 (br. *s*, 4 H, 2 H–C(2′), 2 H–C(6′)); 1.57* (*quint.*, J = 5.5, 2 CH_2(3′), 2 CH_2(5′)); 1.43* (br. *s*, 2 CH_2(4′)); 1.08 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 76.3 (C(2), C(3)); 67.1 (C(1), C(4)); 56.3 (2 C(2′), 2 C(6′)); 26.4 (2 C(3′), 2 C(5′)); 25.6 (CH_3–C(2), CH_3–C(3)); 23.9 (2 C(4′)). ^{13}C-NMR (75 MHz, CD_3OD): 78.2 (C(2), C(3)); 67.7 (C(1), C(4)); 57.3 (2 C(2′), 2 C(6′)); 27.5 (2 C(3′), 2 C(5′)); 25.7 (CH_3–C(2), CH_3–C(3)); 24.9 (2 C(4′)). CI-MS (NH_3): 286 (25), 285 (100), 186 (36), 142 (20), 98 (86). EI-MS 188 (19), 187 (20), 143 (8), 98 (100).

*(2*RS*,3*RS*)-2,3-Dimethyl-1,4-di(morpholin-4-yl)butane-2,3-diol* (**11e**) *and (2*RS*,3*SR*)-2,3-Epoxy-2,3-dimethyl-4-(morpholin-4-yl)butan-1-ol* (**12e**). To a soln. of 1.270 g (11.13 mmol) of **9** in 10 ml of THF 2.272 g (26 mmol) of morpholine were added dropwise. The mixture was then stirred for 1 d at r.t. GC: only little product. Thus, stirring was continued at 60° for additional 2 d. After cooling, the soln. was analyzed by GC (phenylmethylsilicone column, 60 → 250° at 5°/min): t_R(**9** and morpholine) 2.5–3.9, t_R(1st product) 19.2, and t_R(2nd product) 32.8 min, 1st/2nd product 5:3. GC (dimethylsilicone column, 60 → 250° at 5°/min): t_R(1st product) 12.4 and t_R(2nd product) 22.8 min. The solvent was evaporated and the residue distilled in a 'Kugelrohr' oven (*Büchi GKR 51*) under high vacuum to give a viscous, oily distillate. The residue (1.9 g) from this distillation was subjected to CC (150 g of SiO_2, Et_2O, then Et_2O/acetone 20:1 → 10:1, then acetone). The fractions containing **12e** and **11e** were rechromatographed (125 g of SiO_2, Et_2O) to yield 215 mg (10%) of **12e** as a colorless oil, followed by a solid which, after recrystallization from acetone, gave 128 mg (7%) of **11e** as colorless crystals.

Data of **11e**: M.p. 126.5–131°. IR (KBr): 3180 (br., OH), 2960, 2850, 2810, 1455, 1305, 1190, 1115, 1070, 1010, 910, 870, 805. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.68 (br. *s*, 2 OH); 3.70 (*m*, 2 CH_2(2′), 2 CH_2(6′)); 3.06 (br. *s*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.61 (*d*, J = 14, 2 H, H–C(1), H–C(4)); 2.47 (br. *s*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.46 (*d*, J = 14, 2 H, H–C(1), H–C(4)); 1.08 (*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (400 MHz, $(CD_3)_2CO$): 6.99 (*s*, 2 OH); 3.59 (*m*, 2 CH_2(2′), 2 CH_2(6′)); 2.99 (br. *s*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.65 (*d*, J = 13.9, 2 H, H–C(1), H–C(4)); 2.40 (br. *m*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.35 (*d*, J = 13.9, 2 H, H–C(1), H–C(4)); 1.04 (*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (400 MHz, D_2O): 3.74 (*m*, 2 CH_2(2′), 2 CH_2(6′)); 2.93 (br. *m*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.83 (*d*, J = 14.8, 2 H, H–C(1), H–C(4)); 2.62 (br. *m*, 4 H, 2 H–C(3′), 2 H–C(5′)); 2.54 (*d*, J = 14.8, 2 H, H–C(1), H–C(4)); 1.15 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 76.8 (C(2), C(3)); 67.2 (2 C(2′), 2 C(6′)); 66.6 (C(1), C(4)); 55.3 (2 C(3′), 2 C(5′)); 25.7 (CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, D_2O): 80.4 (C(2), C(3)); 69.7 (2 C(2′), 2 C(6′)); 68.0 (C(1), C(4)); 57.3 (2 C(3′), 2 C(5′)); 26.5 (CH_3–C(2), CH_3–C(3)). ^{1}H,^{13}C-COSY (400 MHz, $CDCl_3$): cross-peaks at δ(H), δ(C) 1.08, 25.7 (CH_3–C(2), CH_3–C(3)); 2.47, 55.3 (CH_2(3′), CH_2(5′), the second cross-peak was not observed); 2.46, 2.61, 66.6 (CH_2(1), CH_2(4)); 3.70, 67.2 (CH_2(2′), CH_2(6′)). CI-MS (NH_3): 290 (15, $[M + 2]^+$), 289 (96, $[M + 1]^+$), 189 (4), 188 (45, $[M - (CH_2(morpholine)]^+$), 144 (12), 101 (6), 100 (100, $[CH_2(morpholine]^+$), 56 (7). EI-MS: 188 (33, $[M - (CH_2(morpholine)]^+$), 144 (9), 101 (6), 100 (100, $[CH_2(morpholine]^+$), 56 (9). Anal. calc. for $C_{14}H_{28}N_2O_4$ (288.39): C 58.30, H 9.79, N 9.71; found: C 58.22, H 10.35, N 9.52.

Data of **12e**: IR (film): 3440 (br., OH), 2960, 2930, 2860, 1455, 1380, 1300, 1115, 1035, 1010, 865. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.9 (br. *s*, OH); 3.75 (*d*, J = 11.9, 1 H, H–C(1)); 3.72 (*m*, CH_2(2′), CH_2(6′)); 3.52 (*d*, J = 11.9, 1 H, H–C(1)); 2.77 (*d*, J = 13, 1 H, H–C(4)); 2.67 (*d*, J = 13, 1 H, H–C(4)); 2.60 (*m*, 2 H, H–C(3′), H–C(5′)); 2.46 (*m*, 2 H, H–C(3′), H–C(5′)); 1.45 (*s*, CH_3–C(3)); 1.43 (*s*, CH_3–C(2)). ^{1}H-NMR (400 MHz, $(CD_3)_2CO$): 4.13 (br. *s*, OH, exchangeable with D_2O); 3.62 (*d*, J = 11.4, 1 H, H–C(1)); 3.60 (*m*, CH_2(2′), CH_2(6′)); 3.57 (*d*, J = 11.5, 1 H, H–C(1)); 2.61 (*d*, J = 12.8, 1 H, H–C(4)); 2.49 (*m*, 2 H, H–C(3′), H–C(5′)); 2.46 (*d*, J = 12.8, 1 H, H–C(4)); 2.38 (*m*, 2 H, H–C(3′), H–C(6′)); 1.37, 1.34 (2*s*, CH_3–C(3), CH_3–C(2)). ^{1}H-NMR (400 MHz, (D_6)DMSO): 4.85 (*t*, J = 5.5, OH); 3.57 (*t*, J = 4.6, CH_2(2′), CH_2(6′)); 3.47 (*d*, J = 5.4, CH_2(1)); 2.52 (*d*, J = 12.8, 1 H, H–C(4)); 2.40 (*m*, 2 H, H–C(3′), H–C(5′)); 2.35 (*d*, J = 12.8, 1 H, H–C(4)); 2.31 (*m*, 2 H, H–C(3′), H–C(5′)); 1.31, 1.28 (2*s*, CH_3–C(3), CH_3–C(2)). ^{13}C-NMR (101 MHz, $CDCl_3$): 67.0 (C(1)); 66.6 (C(2′), C(6′)); 64.9* (C(2)); 64.7 (C(4)); 62.8* (C(3)); 54.0 (C(3′), C(5′)); 21.5 (CH_3–C(3)); 17.2 (CH_3–C(2)). ^{13}C-NMR (101 MHz, CD_3COCD_3): 67.4 (C(2′), C(6′)); 65.5 (C(1)); 64.2, 63.3 (C(2), C(3)); 62.9 (C(4)); 54.9 (C(3′), C(5′)); 18.9 (CH_3–C(3)); 16.9 (CH_3–C(2)). ^{1}H,^{13}C-COSY (400/101 MHz, $CDCl_3$): cross-peaks at δ(H), δ(C) 1.43, 17.2 (CH_3–C(2)); 1.45, 21.5 (CH_3–C(3)); 2.46, 2.60, 54.0 (CH_2(3′), CH_2(5′)); 2.67, 2.77, 64.7 (CH_2(4)); 3.72, 66.6 (CH_2(2′), CH_2(6′)); 3.52, 3.75, 67.0 (CH_2(1)). CI-MS (NH_3): 203 (11, $[M + 2]^+$), 202 (100, $[M + 1]^+$), 144 (5), 101 (3, $[M - (CH_2(morpholine)]^+$), 100 (56, $[CH_2(morpholine)]^+$). EI-MS: 186 (2), 144 (6), 101 (7, $[M - (CH_2(morpholine)]^+$), 100 (100, $[CH_2(morpholine]^+$), 56 (11), 43 (11). Anal. calc. for $C_{10}H_{19}NO_3$ (201.27): C 59.68, H 9.52, N 6.96; found: C 58.95, H 10.02, N 7.35.

*(2*RS*,3*RS*)-1-Azido-3,4-epoxy-2,3-dimethylbutan-2-ol* (**10f**), *(2*RS*,3*RS*)-1,4-Diazido-2,3-dimethylbutane-2,3-diol* (**11f**), *and (2*RS*,3*SR*)-4-Azido-2,3-epoxy-2,3-dimethylbutan-1-ol* (**12f**). To a soln. of 0.899 g (7.88 mmol) of **9** in 5 ml of acetone, 2.306 g (35.47 mmol) of NaN_3 in 25 ml of acetone/H_2O 1:1 were added at −22° under vigorous stirring (GC monitoring). After 10 h, the mixture was allowed to warm up to r.t. and stirred for additional 10 h.

After extraction with 5 × 10 ml of Et_2O and drying (Na_2SO_4), the solvent and excess **9** were removed by distillation through a 30-cm *Vigreux* column. GC (5% phenylmethylsilicone, 60 → 250° at 5°/min) of the crude mixture (851 mg): **10f** (t_R 8.2 min), **11f** (t_R 9.5 min), and **12f** (t_R 16.2 min) in a ratio of 14:10:1. Separation was achieved by CC (100 g of SiO_2, pentane/Et_2O 4:1 → 1:4). The yellowish residue of the pentane/Et_2O 1:1 fractions was bulb-to-bulb distilled (75°/high vacuum): 192.7 mg (16%) of **10f** as a colorless oil. The residue of this distillation crystallized spontaneously. The crystals were collected, and the filtrate was evaporated under high vacuum. A second crop of solid material was obtained. Recrystallization from Et_2O/pentane afforded 19.5 mg (1.2%) of **11f** as colorless crystals. Later fractions of the CC gave, after high-vacuum distillation, 320 mg of **12f** (26%) as colorless oil.

Data of **10f**: IR (film): 3480 (br., OH), 2990, 2950, 2100 (N_3), 1450, 1390, 1290, 1140, 1070, 855. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.50 (*d*, *J* = 12.6, 1 H, H–C(1)); 3.33 (*d*, *J* = 12.6, 1 H, H–C(1)); 2.93 (*dq*, *J* = 4.9, 0.7, 1 H, H–C(4)); 2.66 (*d*, *J* = 0.8, 1 H, OH, exchangeable with D_2O); 2.51 (*d*, *J* = 4.9, 1 H, H–C(4)); 1.37 (*d*, *J* = 0.7, CH_3–C(3)); 1.27 (*d*, *J* = 0.8, CH_3–C(2)). ^{13}C-NMR (101 MHz, $CDCl_3$): 71.8 (C(2)); 60.2 (C(3)); 58.2 (C(1)); 49.9 (C(4)); 21.8 (*C*H_3–C(2)); 17.6 (*C*H_3–C(3)). ^{1}H,^{13}C-COSY (400/101 MHz, $CDCl_3$): cross-peaks at δ(H), δ(C) 1.37, 17.6 (*CH*$_3$–C(3)); 1.27, 21.8 (*CH*$_3$–C(2)); 2.51, 2.93, 49.9 (CH_2(4)); 3.33, 3.50, 58.2 (CH_2(1)). CI-MS (NH_3): 176 (6), 175 (100, $[M + NH_4]^+$), 130 (20), 112 (20), 101 (16), 100 (13), 84 (13), 74 (13), 70 (28), 58 (12), 56 (9), 43 (45). EI-MS: 144 (2), 87 (19), 58 (23), 43 (100).

Data of **11f**: M.p. 88.6–90.3°. IR (KBr): 3420 (br., OH), 2990, 2950, 2110 (N_3), 1390, 1370, 1345, 1290, 1230, 1160, 1105, 955, 940. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.65 (*d*, *J* = 12.4, 2 H, H–C(1), H–C(4)); 3.28 (*d*, *J* = 12.4, 2 H, H–C(1), H–C(4)); 2.80 (*s*, 2 OH); 1.22 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 75.9 (C(2), C(3)); 57.2 (C(1), C(4)); 20.4 (*C*H_3–C(2), *C*H_3–C(3)). CI-MS (NH_3): 218 (23, $[M + NH_4]^+$), 201 (26, $[M + 1]^+$), 118 (12), 74 (100), 43 (13). EI-MS: 144 (6), 100 (4), 88 (12), 87 (26), 74 (6), 58 (36), 43 (100). Anal. calc. for $C_6H_{12}N_6O_2$ (200.20): C 36.00, H 6.04, N 41.98; found: C 36.28, H 6.11, N 41.68.

Data of **12f**: IR (film): 3440 (br., OH), 3000, 2970, 2930, 2880, 2100 (N_3), 1460, 1385, 1285, 1035, 855. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (br. *d*, *J* = 11.4, 1 H, H–C(1)); 3.68 (br. *d*, *J* = 11.4, 1 H, H–C(1)); 3.60 (*d*, *J* = 13, 1 H, H–C(4)); 3.44 (*d*, *J* = 13, 1 H, H–C(4)); 2.03 (br. *s*, OH); 1.46, 1.43 (2*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (101 MHz, $CDCl_3$): 65.0 (C(1)); 64.5, 63.5 (C(2), C(3)); 55.3 (C(4)); 17.9, 16.7 (*C*H_3–C(2), *C*H_3–C(3)). CI-MS (NH_3): 176 (2), 175 (35, $[M + NH_4]^+$), 130 (100), 112 (92), 100 (43), 98 (23), 96 (11), 86 (20), 84 (20), 74 (14), 70 (51), 69 (19), 58 (47), 56 (18), 43 (20). EI-MS: 101 (4), 98 (5), 86 (4), 75 (13), 58 (13), 57 (28), 43 (100), 41 (14). Anal. calc. for $C_6H_{11}N_3O_2$ (157.17): C 45.85, H 7.05, N 26.73; found: C 45.37, H 7.29, N 27.13.

*(2*RS*,3*SR*)-3,4-Epoxy-2,3-dimethyl-1-(phenylthio)butan-2-ol* (**10g**) *and (2*RS*,3*RS*)-2,3-Dimethyl-1,4-bis(phenylthio)butane-2,3-diol* (**11g**). To 67 mg (0.59 mmol) of **9** and 0.12 ml (1.2 mmol) of thiophenol at 0°, 10 ml of 0.12M NaOH were added dropwise, and the mixture was stirred at 0° for 1.5 h. The mixture was poured onto ice/H_2O and extracted 3 times with Et_2O. The combined extract was washed with H_2O and sat. NaCl soln., dried (Na_2SO_4), and evaporated and the colorless, oily crude product (200 mg) subjected to CC (20 g of SiO_2, 20 ml of pentane, then 20 ml of pentane/$CHCl_3$ 3:1, finally 200 ml of $CHCl_3$). The colorless oil (140 mg) containing **10g**/**11g** was rechromatographed (25 g of SiO_2, 30 ml of $CHCl_3$ then $CHCl_3$ with 0.05 → 1% Et_2O): 40 mg (20%) of **11g** as colorless crystalline solid and 22 mg (17%) of **10g** as colorless oil.

Data of **10g**: IR (film): 3480 (br., OH), 3080, 3000, 2950, 1590, 1485, 1445, 1390, 1255, 1055, 860, 745, 695. ^{1}H-NMR (90 MHz, $CDCl_3$): 7.5–7.1 (*m*, 5 arom. H); 3.39 (*d*, *J* = 13, 1 H, H–C(1)); 3.14 (*d*, *J* = 13, 1 H, H–C(1)); 2.98 (*d*, *J* = 5, 1 H, H–C(4)); 2.63 (*s*, OH); 2.49 (*d*, *J* = 5, 1 H, H–C(4)); 1.39, 1.36 (2*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (90 MHz, (D_6)DMSO): 7.5–7.1 (*m*, 5 arom. H); 4.77 (*s*, OH); 3.15 (*s*, CH_2(1)); 2.85 (*d*, *J* = 5, 1 H, H–C(4)); 2.45 (*d*, *J* = 5, 1 H, H–C(4)); 1.29, 1.15 (2*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 137.1 (C(1′)); 130.0, 129.0 (C(2′), C(3′)); 126.4 (C(4′)); 71.6 (C(2)); 60.9 (C(3)); 50.4 (C(4)); 45.0 (C(1)); 24.0 (*C*H_3–C(2)); 17.9 (*C*H_3–C(3)). EI-MS: 224 (M^+), 167, 124, 123, 109.

Data of **11g**: M.p. 77.5–78.5°. IR (KBr): 3450 (br., OH), 3080, 3000, 2960, 1590, 1490, 1445, 1390, 1215, 1095, 1060, 1030, 960, 740, 695. ^{1}H-NMR (90 MHz, $CDCl_3$): 7.55–7.1 (*m*, 10 arom. H); 3.57 (*d*, *J* = 13, 2 H, H–C(1), H–C(4)); 3.13 (*d*, *J* = 13, 2 H, H–C(1), H–C(4)); 2.87 (*s*, 2 OH); 1.30 (*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (90 MHz, $(CD_3)_2SO$): 7.5–7.0 (*m*, 10 arom. H); 4.69 (*s*, 2 OH); 3.41 (*d*, *J* = 12.5, 2 H, H–C(1), H–C(4)); 3.15 (*d*, *J* = 12.5, 2 H, H–C(1), H–C(4)); 1.25 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 137.2 (*s*, C(1′)); 129.7* (*d*, C(2′)); 129.0* (*d*, C(3′)); 126.4 (*d*, C(4′)); 76.4 (*s*, C(2), C(3)); 43.4 (*t*, C(1), C(4)); 22.1 (*q*, *C*H_3–C(2), *C*H_3–C(3)). CI-MS (NH_3): 352 (5, $[M + NH_4]^+$), 334 (3, M^+), 318 (14), 317 (68, $[M - OH]^+$), 299 (5), 225 (4), 191 (26), 184 (100), 167 (12), 166 (38), 124 (12), 123 (34).

*(2*RS*,3*SR*)-1-(*tert*-Butylthio)-3,4-epoxy-2,3-dimethylbutan-2-ol* (**10h**) *and (2*RS*,3*RS*)-1,4-Bis(*tert*-butylthio)-2,3-dimethylbutane-2,3-diol* (**11h**). To 135 mg (1.2 mmol) of **9** and 0.16 ml (1.4 mmol) of 1,1-dimethylethanethiol at 0°, 10 ml of 0.12M NaOH were added dropwise, and the mixture was stirred at 0° for 20 min.

The mixture was diluted with 20 ml of ice/H_2O and extracted with Et_2O, the org. layer washed with H_2O and sat. NaCl soln., dried (Na_2SO_4) and evaporated, and the crude product (300 mg) subjected to CC (39 g of SiO_2, Et_2O/petroleum ether 3:7): 84 mg (24%) of **11h** as colorless crystals (after recrystallization from MeOH) and 163 mg (67%) of **10h** as colorless oil.

Data of **10h**: IR (film): 3480 (br., OH), 3070, 2980, 2950, 2910, 2880, 1465, 1370, 1250, 1170, 1110, 1055, 1000, 950, 875, 860. ^{1}H-NMR (90 MHz, $CDCl_3$): 2.97 (*d*, *J* = 12, 1 H, H–C(1)); 2.94 (*dd*, *J* = 5, 0.6, 1 H, H–C(4)); 2.74 (*s*, 1 H, OH); 2.66 (*d*, *J* = 12, 1 H, H–C(1)); 2.45 (*d*, *J* = 5, 1 H, H–C(4)); 1.39 (*d*, *J* = 0.7, CH_3–C(3)); 1.33 (*s*, $(CH_3)_3C$, CH_3–C(2)). ^{1}H-NMR (90 MHz, (D_6)DMSO): 4.53 (*s*, OH); 2.71 (*d*, *J* = 5, 1 H, H–C(4)); 2.65 (*s*, CH_2(1)); 2.43 (*d*, *J* = 5, 1 H, H–C(4)); 1.28* (*s*, CH_3–C(2)); 1.26 (*s*, $(CH_3)_3C$); 1.08* (*s*, CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 70.7 (*s*, C(2)); 60.9 (*s*, C(3)); 50.3 (*t*, C(4)); 42.0 (*s*, $(CH_3)_3C$); 38.4 (*t*, C(1)); 30.9 (*q*, $(CH_3)_3C$); 24.4 (*q*, CH_3–C(2)); 18.0 (*q*, CH_3–C(3)). CI-MS (NH_3): 222 (34, $[M + NH_4]^+$), 205 (48, $[M + 1]^+$), 187 (8, $[M - OH]^+$), 166 (71), 149 (59), 131 (100), 113 (19), 104 (20), 103 (13).

Data of **11h**: M.p. 47.5–49°. IR (KBr): 3500 (br., OH), 2980, 2960, 2940, 2920, 2880, 1465, 1390, 1370, 1220, 1170, 1105, 1055, 960. ^{1}H-NMR (90 MHz, $CDCl_3$): 3.07 (*s*, 2 OH); 3.04 (*d*, *J* = 12, 2 H, H–C(1), H–C(4)); 2.71 (*d*, *J* = 12, 2 H, H–C(1), H–C(4)); 1.32 (*s*, 2 $(CH_3)_3C$); 1.24 (*s*, CH_3–C(2), CH_3–C(3)). ^{1}H-NMR (90 MHz, (D_6)DMSO): 4.17 (*s*, 2 OH); 2.89 (*d*, *J* = 12, 2 H, H–C(1), H–C(4)); 2.59 (*d*, *J* = 12, 2 H, H–C(1), H–C(4)); 1.25 (*s*, 2 $(CH_3)_3C$); 1.16 (*s*, CH_3–C(2), CH_3–C(3)). ^{13}C-NMR (22.63 MHz, $CDCl_3$): 75.4 (*s*, C(2), C(3)); 42.3 (*s*, 2 $(CH_3)_3C$); 37.0 (*t*, C(1), C(4)); 31.0 (*q*, 2 $(CH_3)_3C$); 22.6 (*q*, CH_3–C(2), CH_3–C(3)). CI-MS (NH_3): 295 (41, $[M + 1]^+$), 278 (12), 277 (74, $[M - OH]^+$), 259 (9), 239 (8), 237 (8, $[M - C_4H_9]^+$), 221 (22), 171 (23), 164 (44), 147 (100), 131 (21), 113 (84), 104 (3), 103 (4).

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