Synthesis of Phenyl-Substituted Conduritol B and Its Mechanism of Formation

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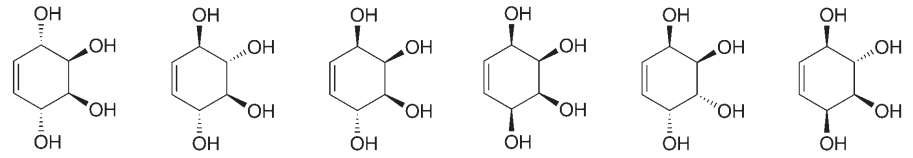
The phenyl-substituted conduritol B **8** was prepared in racemic form in a five-step sequence starting from 2-phenyl-1,4-benzoquinone (**10**) (*Scheme 1*). The reaction mechanism of the key step **12b** → **13** is discussed (*Scheme 2*).

Introduction. – Conduritols are tetrahydroxylated cyclohexene derivatives (for reviews on conduritols, see [1]). The presence of four stereogenic C-atoms in the framework of conduritols allows them to exist as 10 different stereoisomers. Two of them are *meso*-compounds, *i.e.*, conduritol A (**1**) and D (**4**), while the others constitute four pairs of enantiomers, *i.e.*, conduritol B (**2**), C (**3**), E (**5**) and F (**6**). Of these compounds, only conduritol A (**1**) and conduritol F (**6**) are abundant in nature. Conduritols and their derivatives have been found to possess antibiotic, antileukemic, and tumor-inhibitory properties and glycosidase inhibitory activity [1a].

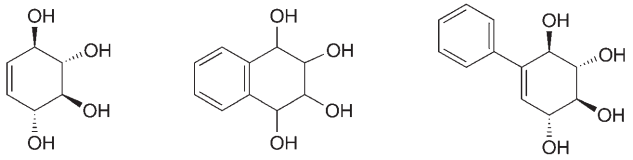


1 Conduritol A | **2** Conduritol B | **3** Conduritol C | **4** Conduritol D | **5** Conduritol E | **6** Conduritol F

Conduritol B (**2**) [2] is the least accessible of the chiral conduritols, because it is the only one that does not possess a *cis*-vicinal-diol pair which can be introduced by *cis*-dihydroxylation reactions. Conduritol B epoxide is a potent, irreversible inhibitor of various plant β-glucosidases [3] and mammalian glucocerebrosidase [4]. It also raises intracellular levels of glucosylceramide by inhibiting glucosylceramidase [5]. Therefore, the synthesis of conduritol B (**2**) and its derivatives is an active area of research. *Haines*, *Taylor*, and co-workers [6] have developed a simple route leading to the synthesis of (±)-conduritol B tetraacetate in three steps starting from *p*-benzoquinone (=cyclohexa-2,5-diene-1,4-dione). These promising results stimulated the study of

[1]) Corresponding author for X-ray crystallography.

benzoconduritol derivatives of the general formula **7** where the C=C bond of the conduritols is formally replaced by an aromatic ring [7], or other ring systems [8][9], which may confer valuable properties to the molecule with such properly located substituents.

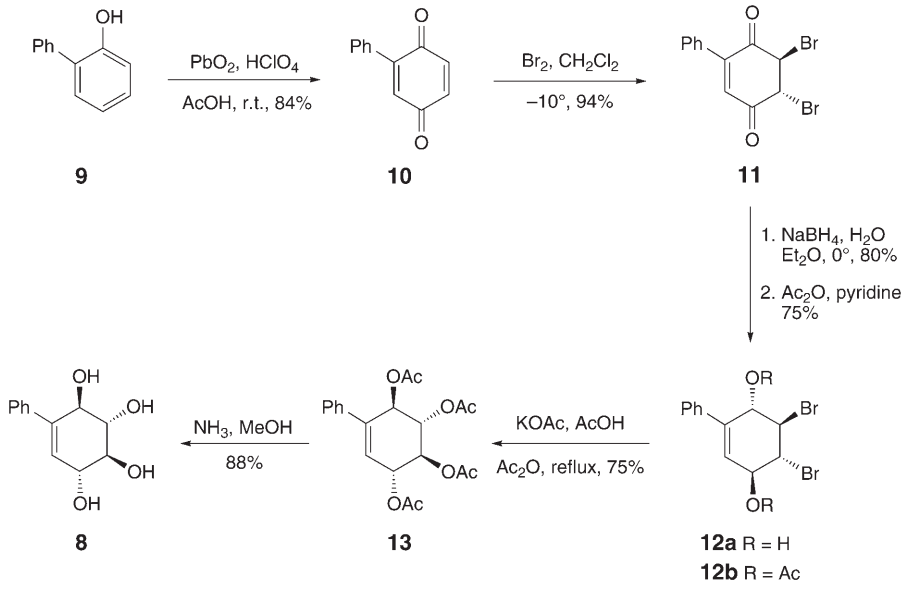


2 **7** **8**

The potential properties of such compounds led us to investigate phenyl-substituted conduritol derivatives. We herein report a novel and efficient synthesis of 5-phenylconduritol B (**8**) starting from a commercially available product, [1,1′-biphenyl]-2-ol (**9**).

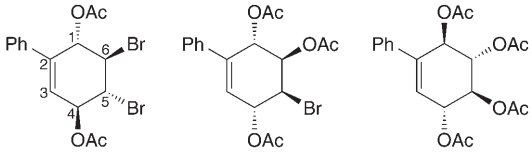
Results and Discussion. – 1. *Synthesis.* The key compound **10** in the synthesis of **8** was synthesized by the oxidation of **9** with PbO_2 in AcOH as described in [10] (*Scheme 1*). The resulting quinone **10** was brominated at low temperature to give only the *trans*-dibromo compound **11** in high yield. The regiospecific addition of Br_2 to the unsubstituted C=C bond can be attributed to the steric effect caused by the Ph substituent and reduced electron density. Reduction of the carbonyl groups in **11** with $NaBH_4$, followed by the acetylation of the OH groups of **12a** with Ac_2O and pyridine

Scheme 1



gave the diacetate **12b**. The ^{1}H- and ^{13}C-NMR spectra, in particular the ^{1}H,^{1}H-coupling constants (*Table 1*), reveal the formation of only one isomer of the diacetate **12b**. An X-ray crystal-structure analysis of **12b** (*Fig. 1*) provided further evidence for the proposed structure.

Table 1. *^{1}H,^{1}H Coupling Constants* [Hz] *for Compounds* **12b**, **13**, *and* **15**[2])



12b **15** **13**

	J(1,6)	*J*(5,6)	*J*(4,5)	*J*(3,4)	*J*(1,3)	*J*(1,4)
12b	6.9	10.8	7.2	2.6	1.9	2.6
15	5.3	2.6	6.3	3.7		
13	6.6	10.2	7.1	2.0	2.0	2.0

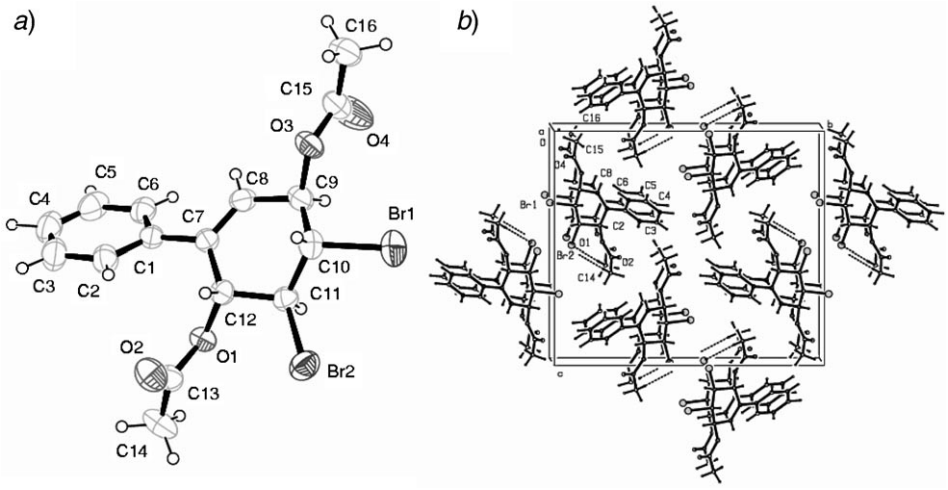


Fig. 1. a) *The molecular structure of* **12b**, *showing the atom-numbering scheme* (arbitrary; thermal ellipsoids at the 50% probability level). b) *Packing diagram and H-bonding geometry.*

The ^{1}H,^{1}H-coupling constant $J(5,6) = 10.8$ Hz of **12b** (*Table 1*), which is consistent with the typical axial/axial coupling constant in a cyclohexene ring, indicates the *trans*-configuration as well as the equatorial/equatorial position of the Br-atoms. Additionally, the coupling constants $J(1,6)$ and $J(4,5)$ confirm the *trans*-(axial/axial) arrangement of the AcO groups and Br-atoms. Also, large long-range coupling constants $J(1,3)$ and $J(1,4)$ of 1.9 and 2.6 Hz, respectively, are observed. Such allylic and homoallylic couplings strongly depend on the conformation of the molecule and generally have values

[2]) For convenience, the atom numbering of **12b**, **13**, and **15** is the same; for systematic names, see *Exper. Part.*

between 0.0–3.0 Hz. Since the homoallylic coupling operates through $\sigma-\pi$ interaction, the dihedral angle also plays an important role. In homoallylic systems, there are two different dihedral angles. When both of these angles are in the range of 90°, the coupling reaches a maximum value [11]. The coupling constant $J(1,4)$ of 2.6 Hz indicates an axial/axial alignment of H–C(1) and H–C(4), *i.e.*, a *trans,-trans,trans*-relationship of the substituents in **12b**.

Compound **12b** was then treated with AcOK and Ac_2O in AcOH in order to substitute the Br-atoms by AcO groups. The obtained product consisted mainly of tetraacetate **13** which was separated by column chromatography (silica gel). The structure of tetraacetate **13** was elucidated on the basis of the ^{1}H- and ^{13}C-NMR spectra in conjunction with 2D-NMR (DEPT-90, HMQC, HMBC, and COSY) experiments. The measured ^{1}H,^{1}H-coupling constants $J(1,6) = 6.6$, $J(4,5) = 7.1$, and $J(5,6) = 10.2$ of **13** (*Table 1*) indicate that the corresponding H-atoms are axially disposed[1]). Thus the relative configuration of **13** was defined as *trans,trans,trans.* An X-ray crystal-structure analysis of **13** confirmed the proposed structure (*Fig. 2*). Removal of the AcO groups by ammonia in MeOH resulted in the formation of conduritol B derivative **8**.

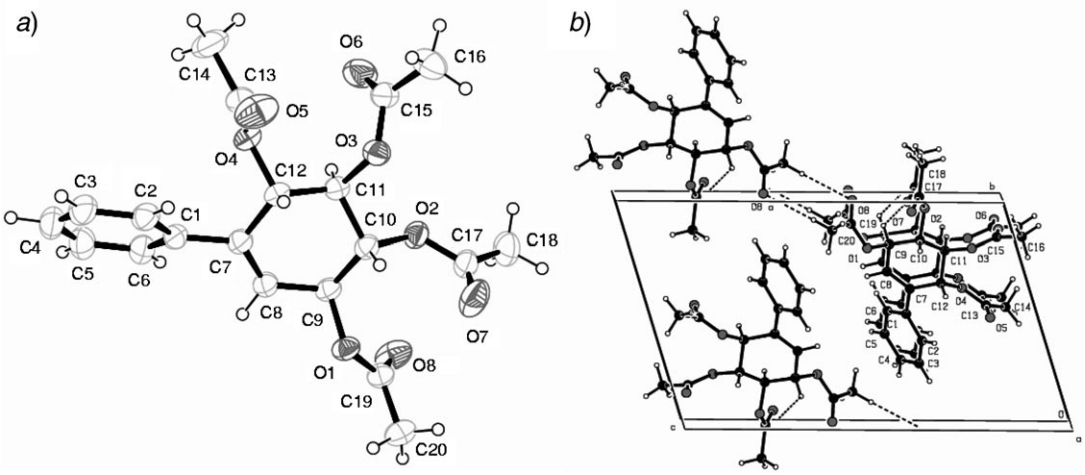
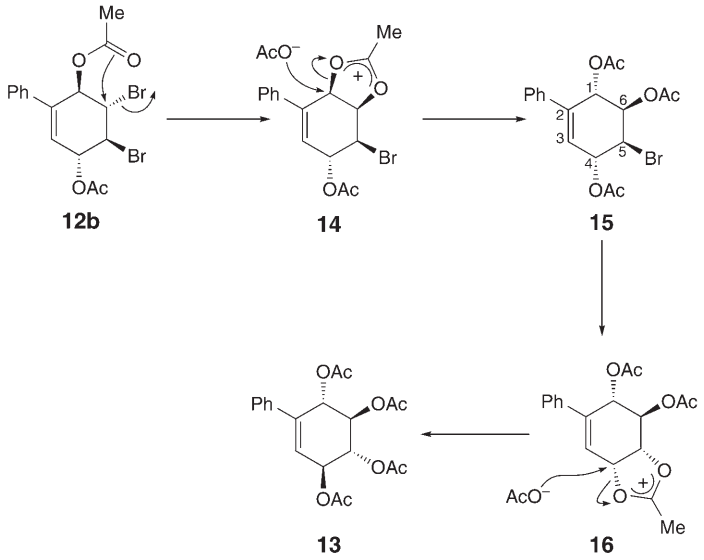


Fig. 2. a) *The molecular structure of* **13***, showing the atom-numbering scheme* (arbitrary; thermal ellipsoids at the 50% probability level). b) *Packing diagram and H-bonding geometry.*

During the transformation of compound **12b** into **13**, a monobromo derivative **15** was formed, in amounts depending on the reaction time (*Scheme 2*). Prolonged reaction times reduced the amount of **15** to 5% or less. Pure **15** was characterized by spectroscopic methods. The formation of this intermediate was important not only in view of the synthetic aspect, but also in view of the mechanism [12] of the transformation of **12b** into **13** where the overall configurations of the substituents were retained. First of all, it was important to figure out the exact position of the Br-atom and the constellation of the AcO groups in **15**. The position of the Br-atom was determined by means of a COSY experiment. The magnitude of the coupling constant $J(5,6) = 2.6$ Hz clearly indicates the *cis*-relation of the Br-atom and AcO group at C(6)[2]). The observed $J(1,6) = 5.3$ and $J(4,5) = 6.3$ Hz establish the *trans*-arrangement of the substituents attached to C(1) and C(4).

Having ascertained the configuration of **15**, we suggest the following mechanism for the formation of **13** from **12b** (*Scheme 2*). The stereospecific synthesis of **13** can be explained by neighboring-group participation [12]. From the structure of the monobromo derivative **15**[3]), it is clear that at first, the carbonyl O-atom of AcO–C(1) attacks C(6) of **12b**. This can be attributed to the possible steric effects between the benzene ring and the AcO group. The formed cyclic oxonium ion **14** undergoes ring opening through attack by acetate ions, most likely at the allylic C-atom to produce the monobromo derivative **15**. The displacement takes place with inversion of the configuration. The observed *cis*-relation of the Br-atom and AcO–C(5)[2]) in **15** can be explained by this mechanism. A second attack by AcO–C(4) at C(5) and formation of a second cyclic oxonium ion **16**, followed by ring opening as described above, produces the tetraacetate **13**, where the configuration of all C-atoms are inverted, compared with those of the dibromo derivative **12b**.

Scheme 2



2. *X-Ray Diffraction Studies.* Compound **12b** crystallized in the monoclinic form with four molecules per unit cell (*Fig. 1,b*). The cyclohexene ring is in a 'twist-chair' conformation, and the puckering parameters of this ring are $Q = 0.514(7)$ Å, $\theta = 129.7(8)^\circ$, and $\phi = 38.5(1)^\circ$, as calculated according to *Cremer* and *Pople* [14]. The two Br-atoms are *trans*-related to each other. The C(10)–Br(1) and C(11)–Br(2) bond lengths are 1.951(3) and 1.448(3) Å, respectively. Furthermore, the AcO moieties are *trans* to each other. Regarding the crystal lattice of **12b** (*Fig. 1,b*), there are no significant intermolecular interactions. The C(14) atom, however is involved in a weak

[3]) *Altenbach* and co-workers have also isolated a similar intermediate during the reaction of 5,6-dibromocyclohex-2-en-1,4-diol diacetate with AcONa/AcOH, however with a different configuration, see [13].

H-bond with Br(2) of a vicinal host molecule (C(14)···Br(2)^a = 3.774(5) Å, C(14)–H···Br(2)^a = 165°, a = –1 + *x*,*y*,*z*). These H-bonded chains propagate along the *a*-axis. Molecules are stacked along the *a*-axis and distances between adjacent successive molecules are 5.318(3) Å.

Compound **13** crystallized in the triclinic form, with two molecules per unit cell (*Fig. 2*,*b*). The cyclohexene ring is in a 'twist chair' configuration like **12b** with the puckering parameters $Q = 0.447(2)$ Å, $\theta = 132.6(3)°$, and $\phi = 49.0(4)°$. The four AcO moieties are *trans*-positioned to each other along the carbocyclic cyclohexene ring. The crystal structure is stabilized through intermolecular H-bonding, involving the vicinal host acetate O- and C-atoms. Two acetate moieties are joined by two C(20)···O(8) (C(20)–H···O(8)^a = 3.538(3) Å, C(20)–H···O(8)^a = 174°, a = 1 – *x*,2 – *y*,1 – *z*) H-bonds, which lead to the formation of a centrosymmetric dimer of the molecule in the crystal unit cell (*Fig. 2*,*b*). The C(9) atom of the cyclohexene is also involved in intermolecular H-bonding with another neighboring acetate O-atom along the *a*-axis (C(9)–H···O(7)^b = 3.241(3) Å, C(9)–H···O(7) = 131°, b = –1 + *x*,*y*,*z*)).

Conclusions. – In summary, with relatively little synthetic effort, we achieved the synthesis of the phenyl-substituted conduritol B **8** in five steps, starting from commercially available [1,1′-biphenyl]-2-ol. In addition, we determined a step-by-step mechanism of the transformation **12b** → **13** with the help of intermediate **15**. We assume that **8** may have important biological activity and may be used as a precursor for the synthesis of other cyclitol derivatives.

Experimental Part

General. TLC: 0.2 mm silica gel *60 F_{254}* aluminium plates (*Merck*). Column chromatography (CC): silica gel (60 mesh; *Merck*). IR Spectra: *Mattson 1000 FT-IR* apparatus; soln. in 0.1 mm cells or KBr pellets; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker Avance-400*; at 400 (^{1}H) and 100 MHz (^{13}C); apparent multiplicities are given in all cases; δ in ppm, *J* in Hz. MS: *Agilent 5975C* apparatus; in *m*/*z* (rel. %).

2-Phenylbenzo-1,4-quinone (=*2-Phenylcyclohexa-2,5-diene-1,4-dione*; **10**) [10]. A soln. of [1,1′-biphenyl]-2-ol (**9**; 10 g, 59 mmol) in AcOH (40 ml) was added dropwise within 10 min to a magnetically stirred, heterogeneous mixture of PbO_2 (35 g, 147 mmol), 70% $HClO_4$ soln. (20 ml), and AcOH (60 ml). The resulting mixture was stirred for 15 min and filtered into a flask containing H_2O (150 ml). The filter cake was washed with CH_2Cl_2 into the same flask. The black powder collected on the filter paper consisted of unreacted PbO_2. The contents of the flask were extracted with CH_2Cl_2. The org. extract was washed with H_2O, dried ($MgSO_4$), and concentrated, and the residue was crystallized from MeOH: **10** (9.0 g, 84%). Deep yellow crystals. M.p. 108–111°. ^{1}H-NMR (400 MHz, $CDCl_3/CCl_4$): 7.49–7.43 (*m*, 5 H); 6.88 (*d*, *A* of *AB*, *J* = 10.1, 1 H); 6.87 (*d*, *J* = 2.2, 1 H); 6.83 (*dd*, *B* of *AB*, *J* = 10.1, 2.2, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3/CCl_4$): 187.0; 186.1; 145.8; 136.9; 136.1; 132.7; 132.6; 130.0; 129.2; 128.4.

rel-*(5*R*,6*R*)-5,6-Dibromo-2-phenylcyclohex-2-ene-1,4-dione* (**11**). To a soln. of **10** (9.0 g, 49 mmol) in CH_2Cl_2 was added dropwise a soln. of Br_2 (7.8 g, 49 mmol) in CH_2Cl_2 at –10° during 1 h. The mixture was stirred at –10° for 1 h and then allowed to warm to r.t. The solvent was evaporated: **11** (15.8 g, 94%). Yellow solid. M.p. 103–105° (from $CHCl_3$). IR ($CHCl_3$): 2934, 1673, 1592, 1348, 1254, 1227, 1162, 1016, 768, 709, 687, 638. ^{1}H-NMR (400 MHz, $CDCl_3/CCl_4$): 7.54–7.45 (*m*, 5 H); 6.78 (*d*, *J* = 1.9, 1 H); 4.93 (*d*, *A* of *AB*, *J* = 2.8, 1 H); 4.87 (*dd*, *B* of *AB*, *J* = 2.8, 1.9, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3/CCl_4$): 187.5; 187.1; 146.7; 132.4; 131.3; 131.0; 129.1; 128.8; 47.1; 45.1. EI-MS: 342, 344, 346 (8, 14, 7, M^+); 262, 263, 264, 265 (25, 29, 28, 27, $[M - Br - H]^+$); 185 (40); 184 (90, $[M - 2\ Br]^+$); 183 (100, $[M - 2\ Br - H]^+$); 157 (30); 156 (75); 135 (45); 127 (35); 102 (65); 82 (55); 63 (25). Anal. calc. for $C_{12}H_8Br_2O_2$: C 41.90, H 2.34; found: C 41.92, H 2.42.

rel-*(1*R*,4*R*,5*S*,6*S*)-5,6-Dibromo-2-phenylcyclohex-2-ene-1,4-diol* (**12a**). To a soln. of **11** (15 g, 44 mmol) in Et_2O (45 ml) cooled to 0° in an ice bath, an aq. $NaBH_4$ soln. (4.1 g, 109 mmol) was added dropwise at 0°. After completion of the reaction (TLC monitoring), the aq. phase was extracted with Et_2O (3 × 50 ml), the combined org. extract dried (Na_2SO_4), and the solvent evaporated: oily **12a** (12.0 g, 80%) which was readily converted to **12b**.

rel-*(1*R*,4*R*,5*S*,6*S*)-5,6-Dibromo-2-phenylcyclohex-2-ene-1,4-diol Diacetate* (**12b**). To a stirred soln. of **12a** (12 g, 35.0 mmol) in pyridine (20 ml), Ac_2O (11.0 g, 105 mmol) was added dropwise at 0°. The mixture was stirred at r.t. for 8 h, then poured into conc. HCl soln. (50 ml) mixture with ice, and extracted with Et_2O (3 × 50 ml). The combined org. extract was washed with $NaHCO_3$ soln. and H_2O and dried ($MgSO_4$), the solvent evaporated, and the residue subjected to CC (SiO_2 (140 g), AcOEt/hexane 18:1). Crystallization from AcOEt/hexane 3:1 gave **12b** (11.0 g, 75%). Pure white crystals. M.p. 114–116°. IR ($CHCl_3$): 2924, 2853, 1772, 1758, 1371, 1194, 1154, 1081, 920, 850, 716. ^{1}H-NMR (400 MHz, $CDCl_3/CCl_4$): 7.32–7.22 (*m*, 5 H); 6.33 (*ddd*, *J* = 6.9, 1.9, 2.6, 1 H); 5.86 (*dd*, *J* = 1.9, 2.6, 1 H); 5.80 (*dt*, *J* = 7.2, 2.6, 1 H); 4.41 (*dd*, *A* of *AB*, *J* = 10.8, 6.9, 1 H); 4.39 (*dd*, *B* of *AB*, *J* = 10.8, 7.2, 1 H); 2.12 (*s*, 3 H); 1.86 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3/CCl_4$): 169.3; 169.2; 140.3; 136.7; 128.5; 128.4; 126.6; 125.8; 73.7; 72.3; 52.7; 51.4; 20.7; 20.5. Anal. calc. for $C_{16}H_{16}Br_2O_4$: C 44.47, H 3.73; found: C 44.44, H 3.62.

rel-*(1*R*,2*S*,3*S*,4*R*)-5-Phenylcyclohex-5-ene-1,2,3,4-tetrol Tetraacetate* (**13**). A vigorously stirred mixture of **12b** (10 g, 23 mmol) in AcOH (150 ml), Ac_2O (30 ml), and anh. AcOK (13.8 g, 140 mmol) was refluxed for 3 days under N_2. The solvent was evaporated, MeOH (20 ml) added to the residue, and the mixture stirred for 10 min. The soln. was concentrated, and the residue was partitioned between Et_2O (50 ml) and H_2O (75 ml). The org. layer was washed with aq. $NaHCO_3$ soln., dried ($MgSO_4$) and concentrated, the solid residue subjected to CC (silica gel, AcOEt/hexane 1:9), and the product crystallized from AcOEt/hexane 3:1: **13** (6.0 g, 75%). Colorless crystals. M.p. 130–132°. IR (KBr): 2995, 1734, 1363, 1217, 1018, 964, 927, 766, 705. ^{1}H-NMR (400 MHz, $CDCl_3/CCl_4$)[1]): 7.28–7.20 (*m*, 5 H); 6.29 (*dt*, *J* = 6.6, 2.0, 1 H); 5.83 (*t*, *J* = 2.0, 1 H); 5.73 (*dt*, *J* = 7.1, 2.0, 1 H); 5.47 (*dd*, *A* of *AB*, *J* = 10.2, 7.1, 1 H); 5.40 (*dd*, *B* of *AB*, *J* = 10.2, 6.6, 1 H); 2.09 (*s*, 3 H); 2.07 (*s*, 3 H); 2.05 (*s*, 3 H); 1.80 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3/CCl_4$): 170.6; 170.5; 170.2; 170.1; 139.4; 136.6; 128.7; 128.6; 126.6; 125.5; 72.5; 71.9; 71.1; 71.0; 21.1; 20.9; 20.8; 20.7. EI-MS: 390 (M^+), 270 (10), 229 (10), 228 (50), 187 (30), 186 (100), 158 (25), 157 (20). Anal. calc. for $C_{20}H_{22}O_8$: C 61.53, H 5.68; found: C 61.06, H 5.68.

rel-*(1*R*,2*S*,3*R*,4*S*)-3-Bromo-6-phenylcyclohex-5-ene-1,2,4-triol Triacetate* (**15**). As described for **13**, with **12b** (5 g, 12 mmol), AcOH (75 ml), Ac_2O (15 ml), and anh. AcOK (6.9 g, 70 mmol) for 36 h. Workup with MeOH (10 ml), Et_2O (50 ml), and H_2O (75 ml), CC, and crystallization as described for **13** gave **15** (3.3 g, 70%). Colorless crystals. M.p. 144–145.5°. IR ($CHCl_3$): 2357, 1745, 1549, 1219, 1020, 926, 749, 704. ^{1}H-NMR (400 MHz, $CDCl_3/CCl_4$)[1]): 7.20–7.35 (*m*, 5 H); 6.07 (*m*, 2 H); 5.70 (*dd*, *J* = 6.3, 3.7, 1 H); 5.40 (*dd*, *J* = 5.3, 2.6, 1 H); 4.40 (*dd*, *J* = 6.3, 2.6, 1 H); 2.20 (*s*, 3 H); 2.15 (*s*, 3 H); 1.91 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3/CCl_4$): 169.3; 169.0; 168.9; 138.9; 136.6; 128.6; 128.5; 126.2; 124.7; 71.4; 71.3; 68.3; 47.2; 20.8; 20.6; 20.5. Anal. calc. for $C_{18}H_{19}BrO_6$: C 52.57, H 4.66; found: C 52.94, H 4.58.

rel-*(1*R*,2*S*,3*S*,4*R*)-5-Phenylcyclohex-5-ene-1,2,3,4-tetrol* (**8**). A soln. of **13** (5.0 g, 13 mmol) in abs. MeOH (40 ml) was stirred for 2 h at r.t. while dry NH_3 was passed through the soln. Evaporation of MeOH and formed acetamide, and crystallization from EtOH/hexane 5:1 gave **8** (2.5 g, 88%). White solid. M.p. 132–135°. IR (KBr): 3352, 2990, 2214, 2071, 1121, 972, 822. ^{1}H-NMR (400 MHz, D_2O): 7.33 (br. *s*, 5 H); 5.71 (*s*, 1 H); 4.70 (br. *s*, 4 OH, 1 H); 4.27 (*d*-like, *J* = 7.0, 1 H); 3.64 (*dd*, *A* of *AB*, *J* = 10.5, 7.0, 1 H); 3.52 (*dd*, *B* of *AB*, *J* = 10.5, 7.5, 1 H). ^{13}C-NMR (100 MHz, D_2O): 139.6; 138.3; 128.6; 128.1; 127.8; 127.1; 75.8; 75.0; 72.3; 72.1. Anal. calc. for $C_{12}H_{14}O_4$: C 64.86, H 6.35; found: C 64.46, H 6.60.

X-Ray Structure Determination. The crystal-structure determination was performed with single crystals of **12b** and **13**. For data collection, a four-circle *Rigaku R-AXIS RAPID-S* diffractometer equipped with a two-dimensional area IP detector was used. The cylindrically shaped imaging plate covered the 2θ angular range between −60 and 140° with a crystal-film distance of 127.4 mm. The graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and oscillation-scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Images were taken successfully by varying ω with three sets of different χ and φ values. The 107 images for three different runs covering *ca.* 99.8% of the *Ewald* spheres were performed. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for *Lorentz* and

polarization effects, and cell refinement were performed by using CrystalClear (*Rigaku/MSC Inc.*, 2005) software [15]. The structures were solved by the direct method with SHELXS [16]. The positional and atomic displacement parameters were refined by the full-matrix least-squares method with SHELXL [16]. The positional and isotropic atomic displacement parameters of H-atoms were refined together with other structural parameters by the full-matrix least-squares procedure based on the squared value of the structure factors. H-Atom positions were calculated from assumed geometries. H-Atoms were included in structure-factor calculations, but they were not refined. The isotropic displacement parameters of the H-atoms were approximated from the U(eq) value of the atom that they were bonded to. The final difference *Fourier* maps showed no peaks of chemical significance. The details of the data collection and final refinement parameters are listed in *Table 2*.

Table 2. *Crystal Data and Structure Refinement of* **12b** *and* **13**

	12b	**13**
Chemical formula	$C_{20}H_{22}O_8$	$C_{16}H_{16}O_4Br_2$
M_r	390.4	432.1
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	triclinic, *P*-1	monoclinic, *P*21/*c*
Unit cell dimensions [Å or °, resp.]	$a = 5.5527(2)$	$a = 5.3179(2)$
	$b = 10.8070(4)$	$b = 19.3018(6)$
	$c = 17.6672(6)$	$c = 16.7417(5)$
	$\alpha = 71.42(4)$	
	$\beta = 96.03(5)$	$\beta = 81.38(5)$
	$\gamma = 84.64(4)$	
Volume [Å^3]	992.4(2)	1709.1(2)
Z	2	4
Density (calc.) [Mg/m^3]	1.31	1.68
Absorption coefficient [mm^{-1}]	0.102	4.757
F(000)	412	856
Crystal size [mm^3]	0.20, 0.17, 0.15	0.23, 0.20, 0.17
θ Range for collection [°]	2.5–30.7	2.4–23.3
Index ranges	$-7 \le h \le 7$	$-5 \le h \le 5$
	$-15 \le k \le 15$	$-21 \le k \le 21$
	$-25 \le l \le 25$	$-18 \le l \le 18$
Refl. collected	54775	22413
Independent refl.	6051 ($R_{int} = 0.047$)	2451($R_{int} = 0.054$)
Observed refl.	5788 ($I > 2\sigma(I)$)	2354 ($I > 2\sigma(I)$)
Parameters	278	239
Goodness-of-fit on F^2	1.35	1.30
Final R indices ($I > 2\sigma(I)$)[a])	$R_1 = 0.082$, $wR_2 = 0.184$	$R_1 = 0.061$, $wR_2 = 0.111$
R Indices (all data)	$R_1 = 0.086$, $wR_2 = 0.187$	$R_1 = 0.064$, $wR_2 = 0.112$
Largest diff. peak and hole [Å^{-3}]	0.256 and 0.198	0.566 and 0.670

[a]) $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, wR_2 = \left\{ \sum \left[w\left(F_0^2 - F_c^2\right)^2 \right] / \sum \left[w\left(F_0^2\right)^2 \right] \right\}^{1/2}$.

CCDC-653894 (**12b**) and CCDC-653895 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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