Chem. Ber. **119**, 464–471 (1986)

# Dichlorocyclopropanation, Epoxidation, and Subsequent Reactions of Isotetralin Derivatives

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Received June 13, 1985

Reaction of excess $CCl_2$ with isotetralin (**1**) gives a separable mixture of bis- and tris-adducts **3**–**6**, where **6** exhibits *syn*-standing dichlorocyclopropanes at a six-membered ring. – Epoxidation of **2a** and **b** furnishes the symmetrical diepoxides **7a** and **b**. With $BuLi/CO_2$, **7b** afforded the α-bromo lactone **10**. – From **3** the epoxide **8** is formed which is cleaved to give the diol **11**. – The epoxide **9a** proves the *anti*-structure of **4**. – $LiAlH_4$ reduction of **3** leads by *exo*-attack mainly to a separable mixture of **13** and **14**.

**Dichlorcyclopropanierung, Epoxidierung und Folgereaktionen von Isotetralin-Derivaten**

Reaktion von überschüssigem $CCl_2$ mit Isotetralin (**1**) ergibt ein trennbares Gemisch der Bis- und Tris-Addukte **3**–**6**, von denen **6** ein Derivat mit *syn*-ständigen Dichlorcyclopropanen am Sechsring ist. – Epoxidierung von **2a** und **b** liefert die symmetrischen Diepoxide **7a** und **b**. Aus **7b** wird mit $BuLi/CO_2$ das α-Bromlacton **10** erhalten. – Aus **3** wird das Epoxid **8** gebildet, das zum Diol **11** geöffnet wird. – Das Epoxid **9a** beweist die *anti*-Struktur von **4**. $LiAlH_4$-Reduktion von **3** führt durch *exo*-Angriff überwiegend zu einem trennbaren Gemisch von **13** und **14**.

The reaction of isotetralin (**1**) with dihalocarbene to give the mono adducts **2a** and **b** was first described by *Vogel* and coworkers[2,3] on the way to methanocyclodecapentaene. Later on these substances found much interest for some solvolysis[4] and carbenoid insertion[5] reactions. However, some details of the synthesis in view of the formation of bis- and tris-adducts remained unknown[6].

In connection with our investigations of the stereochemistry of $CCl_2$ bis- and tris-addition to cyclic dienes and trienes[7–9] we were interested in the products of further $CCl_2$ addition to **2a**. For the synthesis of **2a** we prefer the phase transfer method, however not using chloroform both as solvent and as reagent, but methylene chloride with only a slight excess of chloroform. This single process gives **2a** in 87% yield, based on converted **1**.

With a large excess of chloroform from **1** a mixture of **3**–**6** (63, 8, 24, and 0.5%) was formed which can be separated by repeated crystallizations and subsequent flash chromatography.

**3** is a bis-adduct with an olefinic double bond, and therefore we assign to it the expected[10] structure with dichlorocyclopropanation of the C-2,3 and C-4a,8a double bonds, of course in *anti*-position. However, we isolated a second bis-adduct in minor amounts which does not exhibit olefinic protons. That means both less reactive double


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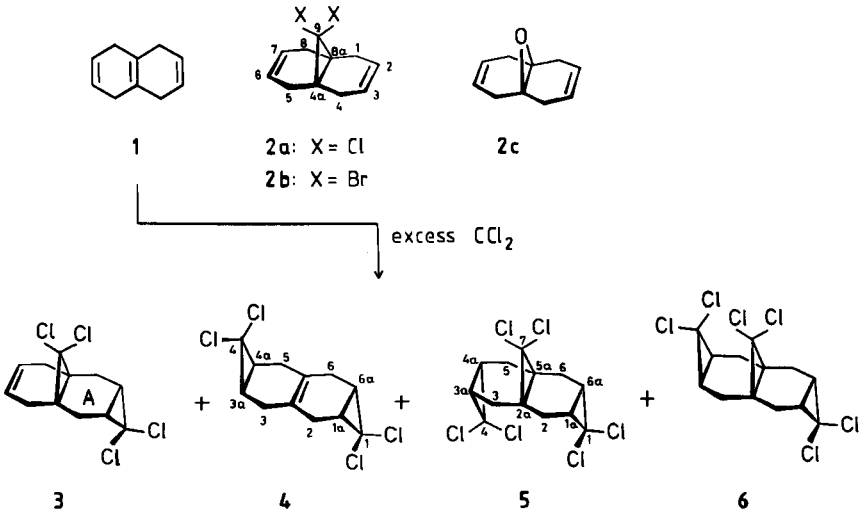
bonds have reacted[11]. The relatively similar chemical shifts for both the protons of the $CH_2$ groups ($\delta$ = 2.03, 2.22, $J$ = 16 Hz) are in good agreement with the *anti*-structure. Furthermore, only the *anti*-bis-adduct **4** should survive a further attack of $CCl_2$ since the tris-adduct from **4** must have the unfavored *syn*-structure **6**, while a hypothetical *syn*-2,3;6,7-bis-adduct would easily react to give **5**. Conclusive evidence for the *anti*-structure of **4** could be derived from the epoxidation reaction (see below).

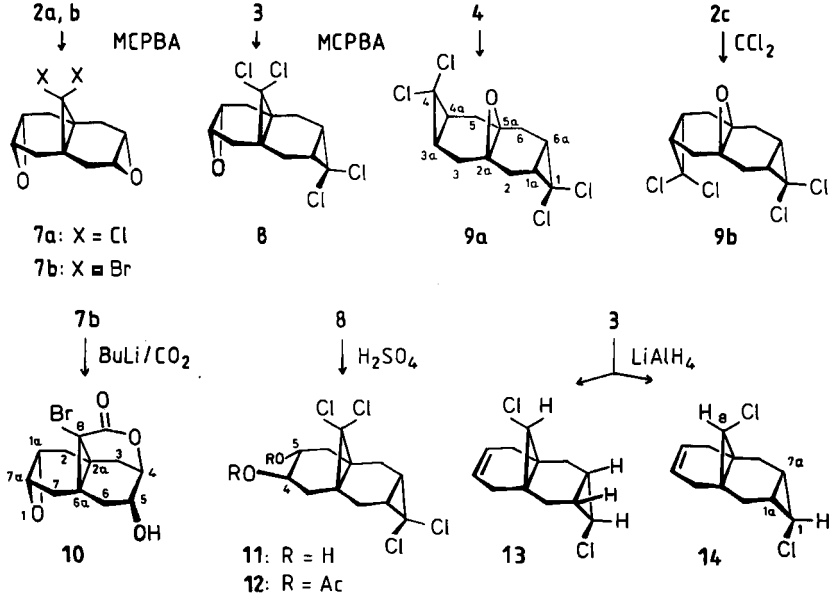



The *anti,anti*-structure of the main tris-adduct **5** is unequivocally proven by the symmetrical NMR spectra. The $^1H$ NMR spectrum exhibits a simple AA'BB'CC' system for the twelve protons and in the $^{13}C$ NMR spectrum we find only five signals with the expected chemical shifts and multiplicities in agreement with the $C_{2v}$ symmetry. The upfield shift of the protons ($\delta$ = 1.68) on the β-side of **5** by the shielding effect of a second cyclopropane ring with $\Delta\delta$ = 0.27 ppm in comparison to **3** (ring A, $\delta$ = 1.95) is obvious. The α-protons exhibit the same chemical shift ($\delta$ = 2.44) in **3** (ring A) and **5**. The assignment for the C-atoms 1, 4, and 7 is based on the signal ratios of the integrated $^{13}C$ NMR spectrum.

The minor tris-adduct **6** could not be completely separated from **5**, not even by several crystallizations and repeated flash chromatography. But from the purest sample of **6** (with about 15% **5**) we were able to assign both the $^1H$ and $^{13}C$ NMR spectra. The cyclopropane protons of **6** are located in the same range ($\delta$ = 1.65) as the respective ones of **5**. However, as proven by spin decoupling, two sets of $CH_2$ protons are present: one with a chemical shift of $\delta$ = 1.81, 2.52 relatively similar to the $CH_2$ group of **5** (1.68, 2.44), but a second set with a strong upfield shift (1.08, 2.19). These findings are in good agreement with the *syn*-structure of **6**. Further support is given by the $^{13}C$ NMR spectrum of **6** where the signal of *syn*-C-7 is shifted downfield ($\delta$ = 72.1) in comparison to **5** (67.6). All NMR data of **6** are in accordance with an *anti,syn*-tris-adduct of $CCl_2$ to **1** which should possess $C_s$ symmetry. We are particularly interested in such *syn*-

structures[7-9], and to the best of our knowledge compound **6** is the first example of a six-membered ring *syn*-condensed with two dichlorocyclopropane rings.

Epoxidation of both **2a** and **b** with excess *m*-chloroperbenzoic acid (MCPBA) gave the epoxides **7a** and **b** in almost quantitative yields. Again $^1H$ and $^{13}C$ NMR spectra give evidence of the $C_{2v}$ structure. In addition, treatment of **7b** with butyllithium and subsequent reaction with carbon dioxide afforded directly the α-bromo lactone **10** by nucleophilic attack of the carboxylate anion to the protonated epoxide.




From bis-adduct **3** with MCPBA we obtained the oxirane **8** with $C_s$ symmetry as shown by the NMR spectra. Hydrolysis of the epoxide ring with sulfuric acid furnished the very insoluble *trans*-diol **11** the $^1H$ NMR spectrum of which could be completely assigned by extensive spin decoupling. The spectrum of the more soluble diacetate **12** confirms the structure. The coupling constants ($J_{4\beta,5\alpha}$ = 10 Hz) of 4β- and 5α-H show that both RO groups are in an equatorial position, but somewhat distorted, because the signal of 3α-H is strongly shifted upfield (δ = 1.50) and *vice versa* 3β-H downfield (2.68), whereas 6α-,6β-H show nearly the same value: δ = 2.00 and 2.10.

With MCPBA the minor bis-adduct **4** yielded the epoxide **9a**. Due to the very small amounts of isolated **4** we did not obtain enough material to purify **9a** totally, but the $^1H$ NMR spectrum gives evidence for the *syn,anti*-structure. There are two different AB systems for the $CH_2$ groups with δ = 1.64, 2.48 for the *syn*- and 1.81, 2.23 for the *anti*-fused six-membered ring. For comparison we prepared the oxirane **9b** with $C_{2v}$ symmetry via epoxide **2c** as mentioned earlier[12]. As expected the $^1H$ NMR spectrum of **9b** shows only one AB system (δ = 1.76, 2.31) for the four magnetically equivalent $CH_2$ groups.

Treatment of **3** with lithium aluminium hydride afforded two isolable products **13** and **14** (ca. 3:1, $^1$H NMR), each containing two monochlorocyclopropane rings. The NOE difference spectrum of **13** established the *all-cis* geometry of the four cyclopropane protons, because on saturation of 1a-,7a-H a strong NOE was observed on 1-H and 8-H. The signal of *syn*-1-H with $\delta$ = 3.29 as triplet ($J$ = 7 Hz) is found also in the minor compound **14** ($\delta$ = 3.16, $J$ = 7 Hz). Consequently the configuration of C-8 must be reversed. Support is given by an upfield shift of 0.1 ppm for the signal of the olefinic protons of **14** in comparison to **13** and by the NOE difference spectrum (in $C_6D_6$), which shows the *syn*-configuration of 8-H and the olefinic protons: there is no interaction between 8-H and 1a-,7a-H, but a strong NOE between 1-H and 1a-,7a-H of **14**.

The $^1$H NMR spectrum of the crude reduction product shows small amounts of *anti*-1-H (*trans*-coupling of 3 Hz) and of cyclopropane-$CH_2$ ($\delta$ = 0.1). This result shows that the *exo*-attack of $LiAlH_4$ to the outer cyclopropane ring is strongly favored.

Financial support by the *Fonds der Chemischen Industrie* is gratefully acknowledged. – Md. A. H. thanks the *Deutsche Akademische Austauschdienst* (DAAD) for a grant. – We are indebted to Prof. Dr. *E. Vogel*, Köln, for a generous gift of isotetralin.

## Experimental Part

$^1$H NMR ($CDCl_3$, int. TMS): Bruker WH-400. – $^{13}$C NMR ($CDCl_3$, int. TMS, off resonance): Varian CFT-20 and Bruker AM-270. – IR (KBr): Perkin Elmer 225. – MS: Varian MAT 711 (70 eV). All compounds show the typical Cl or Br isotope patterns as well as significant Cl (Br) and HCl (HBr) eliminations. – Melting points (uncorrected): Büchi SMP-20. – Column chromatography (CC): silica gel desactivated with 3% water. – Flash chromatography (FC): Merck silica gel 60, 0.040–0.063 mm. – PE = petroleum ether. – All organic solutions after work-up were dried over $MgSO_4$. – C,H-Analyses: Hewlett-Packard C,H,N-Analyzer. – Room temperature = 20°C. – KRD = Kugelrohr distillation.

*Reaction of 1,4,5,8-Tetrahydronaphthalene (Isotetralin)* (**1**) *with $CCl_2$ (Phase Transfer Method)*

a) *With a Slight Excess of $CHCl_3$ in $CH_2Cl_2$:* To a stirred solution of 13.2 g (0.10 mol) of **1**, 0.30 g of benzyltriethylammonium chloride (BTEAC), and 20 ml of $CHCl_3$ in 200 ml of $CH_2Cl_2$ at 20°C, 15 ml of 50% aqueous NaOH was slowly added dropwise. After 4 h refluxing the mixture was stirred overnight, diluted with 500 ml of water, shaked, and separated. The aqueous layer was extracted twice with $CH_2Cl_2$. The combined organic layers were washed with water and evaporated to give 16.0 g of crude product. Distillation at 85–90°C/12 Torr (KRD) yielded 9.3 g of recovered **1**. The residue was crystallized from methanol to give 5.5 g (87% on converted **1**) of *9,9-dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene* (**2a**), m.p. 81–83°C (lit.[2] 83–84°C; lit.[6] 90–91°C, after several recrystallizations). – $^1$H NMR: $\delta$ = 2.27, 2.55, 5.52 (AA'BB'XX', $J_{AB}$ = 18, $J_{AX}$ = $J_{AX'}$ = 1, $J_{BX}$ = $J_{BX'}$ = 0, $J_{XX'}$ = 11 Hz; 1β,4β,5β,8β-H, 1α,4α,5α,8α-H, 2,3,6,7-H) (lit.[13] m 2.45, s 5.55). – $^{13}$C NMR: $\delta$ = 25.0 (s; C-4a, -8a), 30.5 (t; C-1, -4, -5, -8), 74.3 (s; C-9), 123.4 (d; C-2, -3, -6, -7).

b) *With a Large Excess of $CHCl_3$:* Similarly to the procedure as under a), 13.2 g (0.10 mol) of **1**, 0.50 g of BTEAC, 250 ml of $CHCl_3$, and 100 ml of 50% aqueous NaOH were refluxed for 4 h. After work-up the 32 g of crude product were diluted with $CH_2Cl_2$ to give 7.8 g (20%) of *(1aα,2aα,3aα,4aα,5aα,6aα)-1,1,4,4,7,7-Hexachlorooctahydro-1H,3H-2a,5a-methanodicyclopropa[b,g]naphthalene* (**5**), m.p. 268–270°C (dec.). – $^1$H NMR: $\delta$ = 1.66, 1.68, 2.44 (AA'BB'CC', $J_{AA'}$ = 9, $J_{AB}$ = 1, $J_{AC}$ = 7, $J_{BC}$ = 16, $J_{AB'}$ = 0, $J_{AC'}$ = 2.5 Hz; 1a,3a,4a,6a-,

2β,3β,5β,6β-, 2α,3α,5α,6α-H). – $^{13}$C NMR: δ = 23.2 (t; C-2, -3, -5, -6), 24.0 (s; C-2a, -5a), 25.3 (d; C-1a, -3a, -4a, -6a), 66.1 (s; C-1, -4), 67.6 (s; C-7).

$C_{13}H_{12}Cl_6$ (381.0) Calcd. C 40.99 H 3.18 Found C 40.82 H 3.10

Evaporation of the mother liquor gives a second crop (2.6 g) with about 40% of **3**, 10% of **4**, and 50% of **5** ($^1$H NMR). A third crop (5.5 g) crystallizes on standing (90% of **3** and 10% of **4**, $^1$H NMR). From the mother liquor (15.7 g) a 0.5 g sample is separated by FC with pentane/benzene → benzene → $CHCl_3$.

1. Fraction: *(1aα,2aα,6aα,7aα)-1,1,8,8-Tetrachloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1H-cyclopropa[b]naphthalene* (**3**), m.p. 135 °C. – $^1$H NMR: δ = 1.73, 1.95, 2.44 (AA'BB'CC', $J_{AA'}$ = 9, $J_{AB}$ = 1, $J_{AC}$ = 5.5, $J_{BC}$ = 16, $J_{AB'}$ = 0, $J_{AC'}$ = 2.5 Hz; 1a,7a-, 2β,7β-, 2α,7α-H), 2.20, 2.51, 5.45 (AA'BB'XX', $J_{AB}$ = 16, $J_{XX'}$ = 12, $J_{AX}$ = $J_{AX'}$ = $J_{BX}$ = $J_{BX'}$ = 1 Hz; 3β,6β-, 3α,6α-, 4,5-H). – $^{13}$C NMR: δ = 23.6 (t; C-2, -7), 24.4 (s; C-2a, -6a), 25.0 (d; C-1a, -7a), 30.8 (t; C-3, -6), 64.7 (s; C-1), 71.8 (s; C-8), 122.8 (d; C-4, -5).

$C_{12}H_{12}Cl_4$ (298.0) Calcd. C 48.36 H 4.06 **3**: Found C 48.44 H 3.94
**4**: Found C 48.12 H 4.00

2. Fraction: *(1aα,3aβ,4aβ,6aα)-1,1,4,4-Tetrachloro-1,1a,2,3,3a,4,4a,5,6,6a-decahydrodicyclopropa[b,g]naphthalene* (**4**), m.p. 205 °C. – $^1$H NMR: δ = 1.82, 2.03, 2.22 (AA'BB'CC', $J_{AA'}$ = 9, $J_{AB}$ = 2, $J_{AC}$ = 5, $J_{BC}$ = 16, $J_{AB'}$ = $J_{AC'}$ = 0, $J_{BB'}$ = 2, $J_{BC'}$ = $J_{CC'}$ = 3 Hz; 1a,3a,4a,6a-, 2β,3β,5β,6β-, 2α,3α,5α,6α-H). – $^{13}$C NMR: δ = 24.5 (t; C-2, -3, -5, -6), 25.1 (d; C-1a, -3a, -4a, -6a), 65.4 (s; C-1, -4), 119.7 (s; C-2a, -5a).

3. Fraction: *(1aα,2aα,3aβ,4aβ,5aα,6aα)-1,1,4,4,7,7-Hexachlorooctahydro-1H,3H-2a,5a-methanodicyclopropa[b,g]naphthalene* (**6**), m.p. 225 – 230 °C (dec.), contains about 15% of **5**. – $^1$H NMR: δ = 1.08 (ddd, $J$ = 16, 6.5, and 2.5 Hz; 2β-,6β-H), 1.65 (mc; 1a-,3a-,4a-,6a-H), 1.81 (d, br., $J$ = 16 Hz; 3α-, 5α-H), 2.19 (ddd, $J$ = 16, 6.5, and 2.5 Hz; 2α-,6α-H), 2.52 (ddd, $J$ = 16, 6.5, and 2.5 Hz; 3β-,5β-H). – $^{13}$C NMR: δ = 21.2, 25.7 (2 t; C-2, -3, -5, -6), 25.1 (d; C-1a, -6a), 27.3 (s; C-2a, -5a), 27.4 (d; C-3a, -4a), 66.3 (s; C-1), 67.6 (s; C-4), 72.1 (s; C-7).

*9,9-Dibromo-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene* (**2b**): Similarly to procedure a). 13.2 g (0.10 mol) of **1**, 0.50 g of BTEAC, 38 g (0.15 mol) of $CHBr_3$, 70 ml of $CH_2Cl_2$, and 15 ml of 50% aqueous NaOH were refluxed for 16 h. After work-up the crude product (32 g) was distilled at 60 – 100 °C/6 Torr to remove **1** and $CHBr_3$. The residue was crystallized from PE to give 9.4 g (31%) of **2b**, m.p. 122 – 124 °C (lit.[3] 124 – 125 °C). – $^1$H NMR: δ = 2.40, 2.50, 5.53 (AA'BB'XX', $J_{AB}$ = 18, $J_{AX}$ = $J_{AX'}$ = 1, $J_{BX}$ = $J_{BX'}$ = 0, $J_{XX'}$ = 12 Hz; 1β,4β,5β,8β-, 1α,4α,5α,8α-, 2,3,6,7-H) (lit.[14] 2.10, 2.67, 5.68; 3 s, br.). – $^{13}$C NMR: δ = 25.3 (s; C-4a, -8a), 32.8 (t; C-1, -4, -5, -8), 54.3 (s; C-9), 123.6 (d; C-2, -3, -6, -7) (lit.[15] 53.8).

*Epoxidation of* **2a** *and* **b**

*General Procedure:* To a stirred solution of 15 mmol of **2a** or **b** in 120 ml of dry $CH_2Cl_2$ at 0 °C a solution of 35 mmol of MCPBA in 100 ml of dry $CH_2Cl_2$ was added slowly and dropwise. Stirring was continued for 3 h at 0 °C and 20 h at 20 °C. After filtration the reaction mixture was thoroughly washed several times with saturated solutions of $NaHSO_3$, $NaHCO_3$, and NaCl. After removal of the solvent the residue was crystallized.

*(1aα,2aα,3aα,4aα,5aα,6aα)-7,7-Dichlorooctahydro-2a,5a-methanonaphtho[2,3-b:6,7-b']bisoxirene* (**7a**): 3.2 g (15 mmol) of **2a** gave 3.45 g (93%) of **7a**, m.p. 218 – 220 °C (ether/$CHCl_3$ 1:1). – $^1$H NMR: δ = 2.12, 2.36, 3.06 (AA'BB'CC', $J_{AB}$ = 16, $J_{AC}$ = $J_{BC'}$ = 1, $J_{AC'}$ = 0, $J_{BC}$ = 3, $J_{CC'}$ = 4 Hz; 2β,3β,5β,6β-, 2α,3α,5α,6α-, 1a,3a,4a,6a-H). – $^{13}$C NMR: δ = 22.9 (s; C-2a, -5a), 29.6 (t; C-2, -3, -5, -6), 50.2 (d; C-1a, -3a, -4a, -6a), 72.1 (s; C-7).

$C_{11}H_{12}Cl_2O_2$ (247.1) Calcd. C 53.46 H 4.89 Found C 53.66 H 4.76

*(1aα,2aα,3aα,4aα,5aα,6aα)-7,7-Dibromooctahydro-2a,5a-methanonaphtho[2,3-b:6,7-b']bisoxirene* (**7b**): 4.5 g (15 mmol) of **2b** gave 4.85 g (98%) of **7b**, m.p. 223–225°C (ether). – $^1$H NMR: δ = 2.24, 2.34, 3.07 (AA'BB'CC', $J_{AB}$ = 16, $J_{AC}$ = $J_{BC'}$ = 1, $J_{AC'}$ = 0, $J_{BC}$ = 3, $J_{CC'}$ = 4 Hz; 2β,3β,5β,6β-, 2α,3α,5α,6α-, 1a,3a,4a,6a-H). – $^{13}$C NMR: δ = 23.3 (s; C-2a, -5a), 32.0 (t; C-2, -3, -5, -6), 50.5 (d; C-1a, -3a, -4a, 6a), 53.3 (s; C-7).

$C_{11}H_{12}Br_2O_2$ (336.0) Calcd. C 39.32 H 3.60 Found C 39.60 H 3.49

*Epoxidation of* **3** *to* **8**: According to the general procedure 2.98 g (10 mmol) of **3** and 10 mmol of MCPBA were reacted in 100 ml of $CH_2Cl_2$ for 3 h at 20°C. – After FC with $CH_2Cl_2$ 2.26 g (72%) of *(1aα,2aα,3aα,4aα,5aα,6aα)-4,4,7,7-tetrachlorooctahydro-3H-cyclopropa[6,7]naphth-[2,3-b]oxirene* (**8**) were isolated, m.p. 192°C. – $^1$H NMR: δ = 1.66 (ddd, *J* = 9, 6, and 1.5 Hz; 3a-, 4a-H), 1.79 (dd, *J* = 16 and 1.5 Hz; 3β-, 5β-H), 2.02 (dd, *J* = 16 and 1 Hz; 2β-, 6β-H), 2.34 (ddd, *J* = 16, 4, and 1 Hz; 2α-, 6α-H), 2.45 (ddd, *J* = 16, 6, and 2.5 Hz; 3α-, 5α-H), 3.03 (dd, *J* = 4 and 1 Hz; 1a-, 6a-H). – $^{13}$C NMR: δ = 23.3 (s; C-2a, -5a), 24.1 (t; C-3, -5), 24.8 (d; C-3a, -4a), 29.1 (t; C-2, -6), 50.2 (d; C-1a, -6a), 64.9 (s; C-4), 70.2 (s; C-7).

$C_{12}H_{12}Cl_4O$ (314.0) Calcd. C 45.90 H 3.85 Found C 45.73 H 3.76

*Epoxidation of* **4** *to* **9a**: According to the general procedure 4 mg of **4** and 4 mg of MCPBA were reacted in 1 ml of $CH_2Cl_2$ for 24 h at 20°C. After purification on a SEP-PAK Florisil® cartridge (Waters Assoc.) with pentane/ether 2 mg of *(1aα,2aα,3aβ,4aβ,5aα,6aα)-1,1,4,4-tetrachlorooctahydro-1H,3H-2a,5a-epoxydicyclopropa[b,g]naphthalene* (**9a**) were isolated (contains small impurities), m.p. 145–147°C. – $^1$H NMR: δ = 1.62, 1.72 (2 mc; 1a-, 3a-, 4a-, 6a-H), 1.64 (dd, *J* = 17 and 4 Hz; 2β-, 6β-H), 1.81 (dd, *J* = 16 and 1 Hz; 3β-, 5β-H), 2.23 (ddd, *J* = 16, 6, and 3 Hz; 3α-, 5α-H), 2.48 (ddd, *J* = 17, 6, and 3 Hz; 2α-, 6α-H).

*1,4,5,8-Tetrahydro-4a,8a-epoxynaphthalene* (**2c**): Prepared according to lit.[16], m.p. 62°C (lit.[16] 58–61°C) after purification by FC with pentane/ether (1:1). – $^1$H NMR: δ = 2.36, 2.53, 5.47 (AA'BB'XX', $J_{AB}$ = 16.5, $J_{AX}$ = $J_{AX'}$ = $J_{BX}$ = $J_{BX'}$ = 1, $J_{XX'}$ = 10 Hz; 1-, 4-, 5-, 8-$H_2$, 2-, 3-, 6-, 7-H). – $^{13}$C NMR: δ = 30.8 (t; C-1, -4, -5, -8), 60.1 (s; C-4a, -8a), 122.5 (d; C-2, -3, -6, -7).

*(1aα,2aα,3aα,4aα,5aα,6aα)-1,1,4,4-Tetrachlorooctahydro-1H,3H-2a,5a-epoxydicyclopropa-[b,g]naphthalene* (**9b**): 1.48 g (10 mmol) of **2c**, 30 ml of $CHCl_3$, 0.10 g of BTEAC, and 20 ml of 50% aqueous NaOH were refluxed for 2 h. After work-up as described above 2.60 g (83%) of crude **9b** were isolated. Recrystallization from pentane/ether (1:1) afforded pure **9b**, m.p. 130–135°C (dec.) after darkening above 100°C (lit.[12] 125°C dec.). – $^1$H NMR: δ = 1.66, 1.76, 2.31 (AA'BB'CC', $J_{AA'}$ = 9, $J_{AB}$ = $J_{AB'}$ = 1, $J_{AC}$ = 6, $J_{AC'}$ = 3, $J_{BC}$ = 16 Hz; 1a-, 3a-, 4a-, 6a-H, 2-, 3-, 5-, 6-$H_2$). – $^{13}$C NMR: δ = 23.4 (d; C-1a, -3a, -4a, -6a), 24.3 (t; C-2, -3, -5, -6), 56.8 (s; C-2a, -5a), 65.4 (s; C-1, -4).

*(1aα,2aα,4α,5β,6aα,7aα)-8-Bromooctahydro-4,5-dihydroxy-2a,6a-methanonaphth[2,3-b]-oxirene-8-carboxylic Acid 8,4-Lactone* (**10**): To a stirred solution of 2.0 g (6.0 mmol) of **7b** in 60 ml of THF/ether/PE (4:1:1) at –90°C under $N_2$ 4.3 ml (6.3 mmol) of BuLi (15% in hexane) was added dropwise while maintaining the temp. below –80°C. Stirring was continued at –90°C for 1 h and then 6 g of $CO_2$ (solid, resublimed) were rapidly added. After further stirring at –80°C for 30 min the mixture was allowed to warm to 20°C. Then 200 ml of ether were added and the mixture washed twice with each 50 ml of 2% aqueous NaOH. From the organic phase 1.3 g of **7b** were recovered. – The combined aqueous layers were acidified with dilute HCl at 0°C and extracted twice with ether. The ether phase was washed with water and evaporated. From the crude product some valeric acid was removed by distillation at 60°C/0.02 Torr (KRD). The residue (0.26 g) was crystallized from ether/$CH_2Cl_2$ (1:1) to give 0.16 g (28% on converted **7b**) of **10**, m.p. 208–210°C. – IR: 3500–3300 (OH), 1725 $cm^{-1}$ (lactone). – $^1$H NMR (with

spin decoupling): δ = 2.01 (dd, *J* = 16.5 and 1 Hz; 6β-H), 2.07 (ddd, *J* = 14, 4, and 1 Hz; 3β-H), 2.23 (dd, *J* = 16 and 3 Hz; 7β-H), 2.24 (dd, *J* = 16.5 and 2 Hz; 2β-H), 2.38 (dd, *J* = 16.5 and 2 Hz; 2α-H), 2.43 (dd, *J* = 14 and 2 Hz; 3α-H), 2.44 (dd, *J* = 16 and 3 Hz; 7α-H), 2.63 (dd, *J* = 16.5 and 7 Hz; 6α-H), 3.21 (ddddd, *J* = 4, 3, 3, 2, and 2 Hz; 1a-, 7a-H), 4.09 (ddd, *J* = 7, 5, and 1 Hz; 5α-H), 4.46 (dddd, *J* = 5, 4, 2, and 1 Hz; 4β-H). – $^{13}$C NMR ([D$_6$]DMSO): δ = 23.9, 27.5, 32.1, 36.6 (4 t; C-2, -3, -6, -7), 27.5, 28.6 (2 s; C-2a, -6a), 49.4 (s; C-8), 49.6, 50.1 (2 d; C-1a, -7a), 61.8 (d; C-5), 75.1 (d; C-4), 165.9 (s; CO).

$C_{12}H_{13}BrO_4$ (301.1) Calcd. C 47.86 H 4.35 Found C 47.72 H 4.34

*Hydrolysis of* **8** *to* **11**: A solution of 0.31 g of **8** in 20 ml of acetone was refluxed for 20 h with 0.3 ml of 2 N $H_2SO_4$. After cooling 0.17 g of crystals were filtered off. To the filtrate a small amount of $K_2CO_3$ was added, decanted, and evaporated. 0.16 g of residue were combined with the crystals to give 0.33 g (100%) of *(1aα,2aα,4α,5β,6aα,7aα)-1,1,8,8-tetrachlorooctahydro-2a,6a-methano-1H-cyclopropa[b]naphthalene-4,5-diol* (**11**), m.p. 225 °C. – $^1$H NMR (with spin decoupling): δ = 1.50 (dd, *J* = 14 and 10 Hz; 3α-H), 1.68, 1.72 (AB, $J_{AB}$ = 11 Hz, as dd, *J* = 6 and 4 Hz; 1a-, 7a-H), 1.84 (d, *J* = 16 Hz; 2β-H), 1.98 (d, *J* = 15 Hz; 7β-H), 2.00 (dd, *J* = 15 and 12 Hz; 6α-H), 2.10 (dd, *J* = 15 and 6 Hz; 6β-H), 2.41 (ddd, *J* = 15, 6, and 4 Hz; 7α-H), 2.51 (ddd, *J* = 16, 6, and 4 Hz; 2α-H), 2.68 (dd, *J* = 14 and 7 Hz; 3β-H), 3.34 (ddd, *J* = 12, 10, and 6 Hz; 5α-H), 3.59 (ddd, *J* = 10, 10, and 7 Hz; 4β-H). – $^{13}$C NMR: δ = 23.7, 24.0 (2 t; C-2, -7), 24.5, 24.9 (2 d; C-1a, -7a), 27.8 (s; C-2a, -6a), 38.3, 39.2 (2 t; C-3, -6), 65.2 (s; C-1), 70.2 (s; C-8), 71.1, 71.2 (2 d; C-4, -5).

$C_{12}H_{14}Cl_4O_2$ (332.1) Calcd. C 43.41 H 4.25 Found C 43.34 H 4.18

**11**-*Diacetate* (**12**): A solution of 85 mg of **11**, 65 mg of acetic anhydride, and 75 mg of 4-(dimethylamino)pyridine in 5 ml of $CH_2Cl_2$ was allowed to react for 4 h at 20 °C. Then 20 ml of ether were added, the mixture was washed thoroughly with diluted HCl and $NaHCO_3$ solution and evaporated. 87 mg of **12** remained, m.p. 165 °C ($CH_2Cl_2$). – IR: 1730, 1250, 1230 cm$^{-1}$ (OAc). – $^1$H NMR: δ = 1.66 (dd, *J* = 14 and 9 Hz; 3α-H), 1.68, 1.72 (AB, $J_{AB}$ = 11 Hz, as dd, *J* = 6 and 4 Hz; 1a-, 7a-H), 1.82 (d, *J* = 16 Hz; 2β-H), 1.97 (s; 2 OAc), 2.00 (d; *J* = 16 Hz; 7β-H), 2.02 (dd, *J* = 15 and 12 Hz; 6α-H), 2.17 (dd, *J* = 15 and 6 Hz; 6β-H), 2.39 (ddd, *J* = 16, 6, and 4 Hz; 7α-H), 2.48 (ddd, *J* = 16, 6, and 4 Hz; 2α-H), 2.73 (dd, *J* = 14 and 7 Hz; 3β-H), 4.69 (ddd, *J* = 12, 10, and 6 Hz; 5α-H), 4.96 (ddd, *J* = 10, 9, and 7 Hz; 4β-H). – $^{13}$C NMR: δ = 21.0 (q; OCO*Me*), 23.4 (t; C-2, -7), 24.5, 24.9 (2 d; C-1a, -7a), 27.4 (s; C-2a, -6a), 35.4, 36.3 (2 t; C-3, -6), 65.1 (s; C-1), 70.1, 70.6 (2 d; C-4, -5), 71.4 (s; C-8), 170.1 (s; O*C*OMe).

$C_{16}H_{18}Cl_4O_4$ (416.1) Calcd. C 46.18 H 4.36 Found C 46.02 H 4.28

*Reduction of* **3** *to* **13** *and* **14**: A solution of 0.30 g (1.0 mmol) of **3** in 25 ml of THF was added to 0.10 g (3.0 mmol) of $LiAlH_4$ in 5 ml of ether. After 3 h refluxing a saturated solution of $NH_4Cl$ was added dropwise, the solution was decanted, evaporated, and worked up with $CH_2Cl_2$/water as usual to obtain 0.23 g of crude product (**13**:**14** ca. 3:1, $^1$H NMR). After FC with pentane/10% ether two pure fractions were isolated.

1. Fraction: *(1aα,2aα,6aα,7aα)-endo-1,syn-8-Dichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1H-cyclopropa[b]naphthalene* (**14**), 30 mg, m.p. 58 °C. – $^1$H NMR [$C_6D_6$]: δ = 1.18 [0.81] (ddddd, *J* = 9, 7, 5.5, 2.5, and 1 Hz; 1a-, 7a-H), 1.68 [1.62] (dd, *J* = 15 and 1 Hz; 2β-, 7β-H), 2.12 [2.04] (d, br., *J* = 16 Hz; 3β-, 6β-H), 2.20 [2.15] (ddd, *J* = 15, 5.5, and 2.5 Hz; 2α-, 7α-H), 2.38 [2.10] (dd, *J* = 16 and 2 Hz; 3α-, 6α-H), 3.14 [3.18] (s; 8-H), 3.16 [2.77] (t; *J* = 7 Hz; 1-H), 5.45 [5.26] (AA', *J* = 12 Hz, as dd, *J* = 2 and 1 Hz; 4-, 5-H). – $^{13}$C NMR: δ = 12.9 (d; C-1a, -7a), 21.2 (t; C-2, -7), 21.4 (s; C-2a, -6a), 31.7 (t; C-3, -6), 38.4 (d; C-1), 41.3

(d; C-8), 124.6 (d; C-4, -5). – MS: *m/z* = 230 (6)/228 (8%, $M^+$), 193 (27), 157 (27), 143 (26), 129 (52), 128 (32), 117 (52), 115 (47), 105 (38), 91 (100), 79 (46), 77 (52), 51 (43).

$C_{12}H_{14}Cl_2$ (229.2) Calcd. C 62.90 H 6.16 **14**: Found C 62.75 H 6.07
**13**: Found C 62.88 H 6.09

2. Fraction: *(1aα,2aα,6aα,7aα)-endo-1,anti-8-Dichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1H-cyclopropa[b]naphthalene* (**13**), 0.10 g, m.p. 63 °C. – $^1$H NMR: δ = 1.04 (dddd, *J* = 9, 7, 6, and 4 Hz; 1a-, 7a-H), 1.50 (dd, *J* = 15 and 4 Hz; 2β-, 7β-H), 2.04 (d, br., *J* = 16 Hz; 3β-, 6β-H), 2.20 (ddd, *J* = 15, 6, and 2 Hz; 2α-, 7α-H), 2.27 (d, br., *J* = 16 Hz; 3α-, 6α-H), 3.10 (s; 8-H), 3.29 (t, *J* = 7 Hz; 1-H), 5.56 (AA', br., *J* = 12 Hz; 4-, 5-H). – $^{13}$C NMR: δ = 10.4 (d; C-1a, -7a), 18.7 (s; C-2a, -6a), 23.4 (t; C-2, -7), 27.6 (t; C-3, -6), 39.3 (d; C-1), 42.0 (d; C-8), 124.3 (d; C-4, -5). – MS: *m/z* = 230 (12)/228 (20%, $M^+$), 195 (32), 193 (100), 157 (70), 129 (80), 128 (72), 91 (80).

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[17] **Correction**: X-ray analysis (Prof. *Dr. J. Pickardt,* Institut für Anorganische und Analytische Chemie, Technische Universität Berlin) meanwhile has shown compound **16** (*7,7,10,10-tetrachloro[7.1.0.0$^{6,8}$]decane*) to be the *anti*- instead of the proposed *syn*-isomer.

[135/85]