Highly Strained Cage Compounds from a Fourfold Bridged Tricyclo[4.2.0.0^{2,5}]octa-3,7-diene

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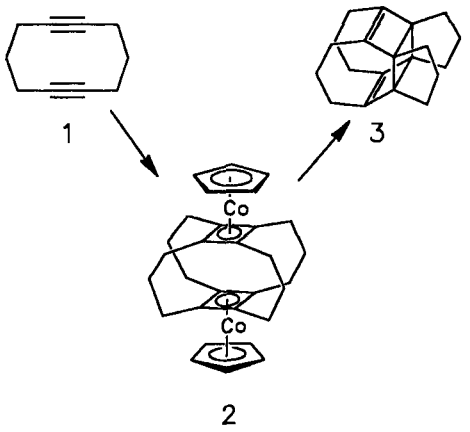
The fourfold bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-diene derivative **3** reacts with diazomethane and *m*-chloroperbenzoic acid (*m*CPBA) to yield the monoadduct **5** in good and the bisadduct **4** in poor yield as well as the mono- and bisepoxides **7** and **8** in good yields, respectively. Also the "mixed" product **6** is obtained. All five compounds are strained propellanes. The X-ray crystallographic structure analysis of **8** reveals a distance of 2.812 Å between the epoxide rings.

Cage compounds have fascinated chemists for many years[1,2]. They are not only appealing because of their usually high symmetry but also represent versatile model compounds. Due to their rigid geometry they are used as models for cycloaddition reactions, for the study of long-range interactions and for the investigation of the geometrical conditions for electron transfer, to name only a few examples.

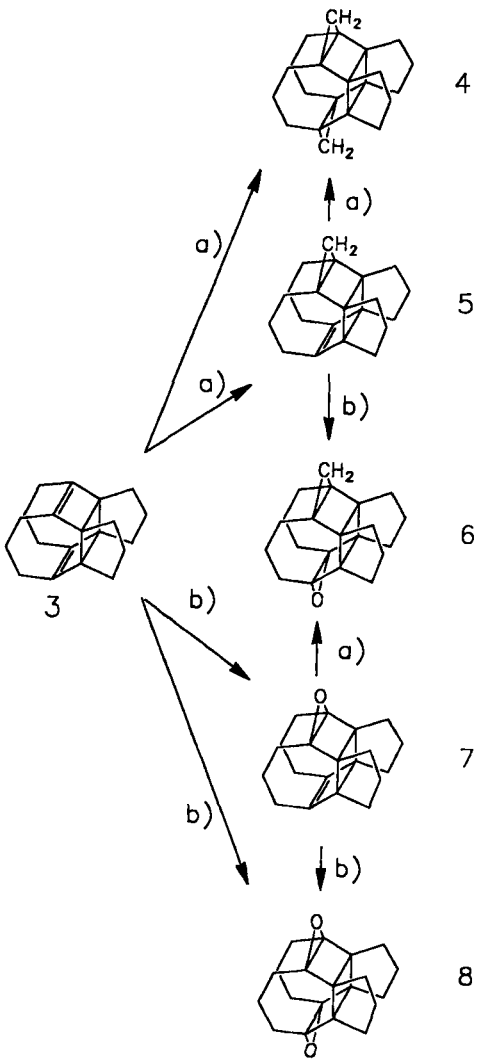


Recently, we have found an easy access to heptacyclo[10.8.0.0^{2,6}.0^{2,11}.0^{6,17}.0^{7,11}.0^{7,16}]eicosa-1(12),16-diene (**3**)[3]. This polycycle can be looked at as a *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene unit which is fourfold bridged by propano moieties. The synthesis of **3** is achieved by oxidation of the superphane **2** with Ce^{IV}. Phane **2** is obtained from 1,6-cyclodecadiyne (**1**) and dicarbonyl (η^5-cyclopentadienyl)-cobalt [CpCo(CO)$_2$][4] or (η^4-1,5 cyclooctadiene) (η^5-cyclopentadienyl)cobalt [CpCo(COD)] in acceptable yields if electron-accepting groups at the Cp rings are used[5]. The low first ionization energy of **3** ($I_{v,1}$ = 7.6 eV)[3] has prompted us to treat **3** with electrophiles such as carbene or *m*-chloroperbenzoic acid (mCPBA). This paper reports on these reactions and describes new highly strained cage compounds.

Results

The reaction of **3** with diazomethane in the presence of catalytic amounts of palladium acetate [Pd(OAc)$_2$][6] yields

Scheme 1



a) = CH_2N_2, $Pd(OAc)_2$; b) = mCPBA

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a mixture of the mono- (**5**) and bisadduct (**4**) in 68 and 3% yield respectively. The products can be separated by column chromatography.

The monoene **5** can be converted into **4** by reaction with diazomethane in the presence of $Pd(OAc)_2$. The reaction of **3** with equimolar amounts of *m*CPBA[7] yields the monoepoxide **7** in 74% yield. The corresponding reaction with two equivalents of *m*CPBA gives the bisepoxide **8** in 92% yield. The monoepoxide **7** can also be converted into the bisepoxide by treatment of **7** with *m*CPBA in excellent (90%) yield. The "mixed" product **6** is obtained either by reaction of **5** with *m*CPBA (75% yield) or by treatment of **7** with diazomethane.

The structural assignment of **4**–**8** is based on the spectroscopic data. For **4**, **5**, and **6** we find in the ^{1}H-NMR spectra the signals for two (**5**,**6**) and four protons at high field ($\delta = -0.12$ to 0.67). In the ^{13}C-NMR spectra the signals for the four trimethylene chains and the quaternary carbon atoms as well as for the olefinic carbon atoms in the case of **5** and **7** are observed.

Since structural investigations on *syn*- or *anti*-tricyclo-[4.2.0.0^{2,5}]-octane derivatives are very rare[8] we have investigated the structural details of **8** by means of an X-ray study. In Figure 1 we show a side view and a top view of one molecule in the crystal.

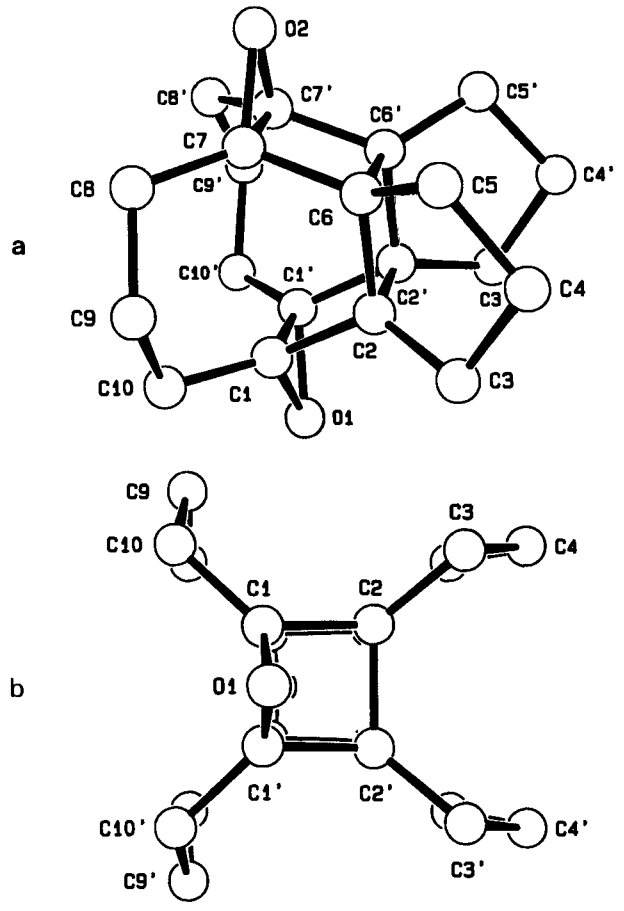

Figure 1 a) Side view and b) top view of the structure of **8** obtained by X-ray structure determination. Bond lengths [Å]: O1–C1 1.460(2), O2–C7 1.459(2), C1–C1′ 1.494(2), C1–C2 1.527(2), C1–C10 1.500(2), C2–C2′ 1.584(2), C2–C3 1.523(2), C2–C6 1.574(2), C3–C4 1.545(2), C4–C5 1.536(2), C5–C6 1.524(2), C6–C7 1.527(2), C6–C6′ 1.593(2), C7–C7′ 1.491(2), C7–C8 1.499(2), C8–C9 1.533(2), C9–C10 1.534(2)

Compound **8** displays a molecular mirror symmetry in the crystal. The molecular geometry shows only negligible deviations from $C_{2v}(mm2)$ symmetry. The interplanar angle between the oxirane rings and their adjacent four-membered rings is 108.7°. The corresponding angle between the central four-membered ring and both neighboring four-membered rings with *syn*-orientation in the tricyclo[4.2.0.0^{2,5}]octane system is 113.9°. Both propano bridges at the oxirane rings are bent away from each other [Figure 1 b; torsional angles: C6–C7–C8–C9 −25.0(2)°, C2–C1–C10–C9 28.7(2)°]. In contrast to this, the other two propano bridges are bent towards each other [C1–C2–C3–C4 −155.3(1)°, C4–C5–C6–C7 156.1(1)°]. The intramolecular nonbonding distance C1···C7 2.812(2) Å is very short. As anticipated the repulsion between the two oxirane units causes an elongation of the four-membered ring bond C2–C6 1.574 Å (Figure 1). Both bridging bonds C2–C2′ 1.584 and C6–C6′ 1.593 Å have the longest distances within the molecule. The bridging bonds C1–C1′ 1.494 Å and C7–C7′ 1.491 Å (Figure 1) are considerably shorter because they also belong to oxirane rings. Oxirane derivatives have C–C distances of the order of 1.47 Å[9].

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Experimental

Melting points are uncorrected. ^{1}H NMR: Bruker AS 200 (200 MHz, $CDCl_3$). – ^{13}C NMR: Bruker AS 200 (50.32 MHz, $CDCl_3$). – IR: Perkin Elmer 580B. – MS: Vacuum Generators ZAB (EI, 70 eV). – Elemental analyses: Mikroanalytisches Labor der Universität Heidelberg.

X-Ray Data of **8**: Orthorhombic space group *Pnma*, $Z = 4$, $a = 8.873(1)$, $b = 11.906(2)$, $c = 14.742(3)$ Å; $D_{calc} = 1.26$ Mg m^{-3}, $\sin\theta/\lambda = 0.66$ Å^{-1}, Enraf Nonius CAD 4 diffraktometer, Mo–K_α radiation, graphite monochromator, ω-2θ scan; 1929 independent reflections, 1419 observed [$I > 2.5\sigma(I)$]; crystal size 0.5 × 0.5 × 0.4

Tab. 1. Atomic coordinates and equivalent thermal parameters U_{eq} of **8**. $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

Atom	x	y	z	$U_{eq} \times 10^3$[Å^2]
O1	0.9477(1)	0.2500	0.2170(1)	37(1)
O2	0.5534(1)	0.2500	-0.1185(1)	42(1)
C1	0.8454(1)	0.3007(1)	0.1444(1)	29(1)
C2	0.9176(1)	0.3037(1)	0.0281(1)	29(1)
C3	1.0468(2)	0.3661(1)	-0.0056(1)	41(1)
C4	1.0321(2)	0.3764(1)	-0.1342(1)	48(1)
C5	0.8632(2)	0.3677(1)	-0.1608(1)	44(1)
C6	0.8007(1)	0.3040(1)	-0.0713(1)	31(1)
C7	0.6365(1)	0.3006(1)	-0.0332(1)	32(1)
C8	0.5506(2)	0.3675(1)	0.0365(1)	40(1)
C9	0.6532(2)	0.4242(1)	0.1128(1)	42(1)
C10	0.7449(2)	0.3697(1)	0.1988(1)	37(1)

mm. Structure solution: MULTAN[10]. Full-matrix refinement: F, C and O atoms refined anisotropically, H atoms isotropically, 151 variables, $R = 0.041$, $\Delta\varrho(\max) = 0.19$ e Å^{-3}; programs: SDP[11]. Atomic coordinates and temperature factors are compiled in Table 1. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-400057, the names of the authors, and the journal citation.

Reaction of **3** *with Diazomethane:* To a cooled solution (−10°C) of 200 mg (0.76 mmol) of **3** in 10 ml of dry THF were added $Pd(OAc)_2$ (2 mg, 0.0089 mmol) and an ethereal solution (10 mmol in 20 ml of ether) of diazomethane. The resulting mixture was allowed to warm up to room temp. and stirred at ambient temp. for 0.5 h. After filtration, the organic solvents were removed, and the residue was purified by chromatography (pentane, silica gel). In addition to starting material **3** (38 mg, 19%) the hydrocarbons **5** (133 mg, 63%) and **4** (6 mg, 3%) are obtained.

5: M.p. 204°C (dec.). – ^{1}H NMR (200 MHz, C_6D_6): δ = −0.12 (d, J = 3.7 Hz, 1H), 0.67 (d, J = 3.7 Hz, 1H), 1.03–1.19 (m, 2H), 1.4–1.68 (m, 16H), 1.94–2.05 (m, 2H), 2.19–2.37 (m, 4H). – ^{13}C NMR (50.32 Hz, C_6D_6): δ = 19.1 (CH_2), 24.3 (CH_2), 26.1 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 27.1 (CH_2), 30.9 (Cq), 53.1 (Cq), 58.2 (Cq), 143.9 (Cq). – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 1649, 1436.

$C_{21}H_{26}$ (278.4) Calcd. C 90.59 H 9.41
Found C 90.34 H 9.43

4: White solid, m.p. 135°C (dec.) – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.04 (d, J = 3.9 Hz, 2H), 0.56 (d, J = 3.8 Hz, 2H), 1.41–1.72 (m, 20H), 2.08–2.18 (m, 4H). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 22.1 (CH_2), 25.2 (CH_2), 25.6 (CH_2), 27.1 (CH_2), 28.0 (CH_2), 31.4 (Cq), 54.0 (Cq). – IR ($CDCl_3$): $\tilde{\nu}$ = 2918 cm^{-1}, 1436.

$C_{22}H_{28}$ Calcd. 292.2191 Found 292.2176 (MS)

Preparation of **7**: To a cooled solution (−78°C) of **3** (76 mg, 0.29 mmol) in 20 ml of CH_2Cl_2 was added during 20 min *m*CPBA (50 mg, 0.29 mmol) in 10 ml of CH_2Cl_2. The reaction mixture was allowed to warm up to room temp., and then the reaction was quenched with 20 ml of aqueous (5%) $NaHCO_3$. After separation of the layers the aqueous one was extracted with ether (3 × 10 ml). The organic phase and the extracts were combined, dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (pentane/ether, 5:1) and yielded 60 mg (74%) of **7** as a colorless solid, m.p. 190°C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24–1.86 (m, 18H), 2.14–2.41 (m, 6H). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 21.9 (CH_2), 24.1 (CH_2), 24.7 (CH_2), 25.9 (CH_2), 26.0 (CH_2), 27.2 (CH_2), 56.2 (Cq), 58.4 (Cq), 69.7 (Cq), 144.0 (Cq). – IR ($CDCl_3$): $\tilde{\nu}$ = 2924 cm^{-1}, 2834, 1640, 1430, 1220, 972, 816.

$C_{20}H_{24}O$ Calcd. 280.1827 Found 280.1764 (MS)

Preparation of **8** *from* **3**: To a cooled solution (−10°C) of **3** (132 mg 0.50 mmol) in 100 ml of ether was added during 1.5 h *m*CPBA (172 mg, 1 mmol) dissolved in 100 ml of ether. The workup was identical with that used for the preparation of **7**. The crude product was purified by column chromatography on silica gel (pentane/ether, 2:1) yielding **8** (136 mg, 92%) as a colorless solid, m.p. 220°C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.48–1.96 (m, 20H), 2.29–2.38 (m, 4H). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 22.0 (CH_2), 24.5 (CH_2) 25.1 (CH_2), 27.0 (CH_2), 58.1 (Cq), 68.9 (Cq). – IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1}, 1432, 1269, 900, 822.

$C_{20}H_{24}O_2$ (296.4) Calcd. C 81.04 H 8.16
Found C 80.94 H 8.23

Preparation of **6** *from* **5**: To a cooled solution (−78°C) of **5** (83 mg, 0.30 mmol) in CH_2Cl_2 was added with stirring *m*CPBA (52 mg, 0.30 mmol) in 10 ml of CH_2Cl_2 during 1 h. The reaction mixture was allowed to warm up to room temp., and stirring was continued for 1.5 h at ambient temp. The workup was the same as that for **7**. The crude product was purified by column chromatography (silica gel, pentane/ether, 2:1) yielding **6** (66 mg, 75%) as a colorless solid, m.p. 210°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.03 (d, J = 3.8 Hz, 1H), 0,58 (d, J = 3.8 Hz, 1H), 1.24–1.81 (m, 20H), 2.09–2.34 (m, 4H). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 21.1 (CH_2), 23.1 (CH_2), 25.4 (CH_2), 25.5 (CH_2), 26.2 (CH_2), 26.4 (CH_2), 26.7 (CH_2), 30.9 (Cq), 53.5 (Cq), 58.3 (Cq), 69.8 (Cq). – IR (KBr): $\tilde{\nu}$ = 2916 cm^{-1}, 1435, 1240, 844.

$C_{21}H_{26}O$ (294.4) Calcd. C 85.67 H 8.90
Found C 85.61 H 8.90

Preparation of **8** *from* **7**: To a cold (0°C) solution of **7** (140 mg, 0.50 mmol) in 100 ml of ether was added 86 mg (0.50 mmol) of *m*CPBA. The reaction mixture was allowed to warm up to room temp. and stirred overnight. The workup was identical with that used for the preparation of **7**. The crude product was purified by chromatography on silica gel (pentane/ether, 2:1) yielding **8** (133 mg, 90%) as a colorless solid.

Preparation of **4** *from* **5**: To a solution of **5** (200 mg, 0.72 mmol) in 10 ml of THF was added at room temp. $Pd(OAc)_2$ (1 mg, 0.0045 mmol) followed by the addition of CH_2N_2 (10 mmol in 20 ml of ether). The mixture was stirred for 1 h at ambient temp. After filtration the solvent was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: pentane) yielding **4** (15 mg, 7%) and **5** (144 mg 72%).

Preparation of **6** *from* **7**: The same procedure was used as for the preparation of **4** from **5**. The following amounts were used: 140 mg (0.50 mmol) of **7** in 10 ml of THF, 1 mg of $Pd(OAc)_2$ (0.0045 mmol), 10 mmol of CH_2N_2 in 20 ml of ether. The purification of the crude product by chromatography (silica gel, pentane/ether, 2:1) yielded **6** (5 mg, 3%) and **7** (121 mg, 86%).

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