Synthesis, Structure, and Properties of Twofold Bridged Sesquinorbornenes

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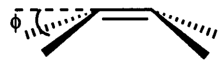
Received April 23, 1998

Keywords: Alkenes / Cycloadditions / Cage compounds / Ab initio calculations / Double-bond pyramidalization

The twofold bridged sesquinorbornenes **2** and **6** were prepared using sequential [4 + 2] cycloadditions of benzoquinone with 1,5-dihydropentalenes **1** and **5**. These syntheses were improved using dilution conditions or a more reactive substituted benzoquinone. Results from semiempirical and ab initio DFT calculations indicated remarkably high pyramidalization angles (ϕ = 46–47°) for the central C–C double-bond atoms. The chemical reactivity with triplet and singlet oxygen, dimethyldioxirane and *N*-methyl-1,2,4-triazoline-3,5-dione supports these structural assignments.

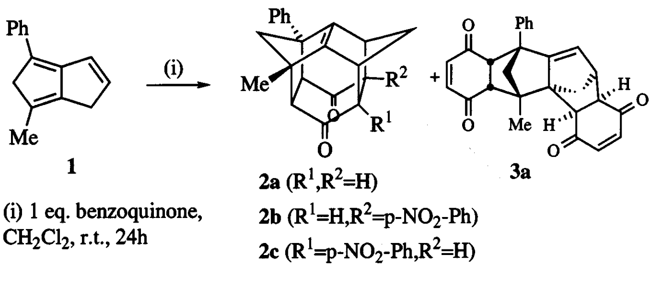
The structural properties and the chemical reactivity of *syn*-sesquinorbornes have been studied intensively[1] in the last decades. Especially the symmetric deformation of the central C−C double bond is a remarkable property which leads to an increased reactivity in comparison with norbornenes. One out of several parameters which are used to describe the out-of-plane deformation is the pyramidalization angle ϕ as defined by Borden[2] ($\cos\phi = -\cos(\mathrm{RCC})/[\cos 0.5(\mathrm{RCR})]$, see Figure 1). Several *syn*-sesquinorbornes have been described with ϕ values up to 25°.[3] Much higher pyramidalization angles have been determined for the fullerene C_{60} ($\phi_{ex.} = 31.6°$),[4] a sesquinorbornatriene ($\phi_{ex.} = 32.4°$)[5] and a secododecahedradiene ($\phi_{ex.} = 35.3°$).[6] The 9,9′,10,10′-tetradehydrodianthracene (**10**), prepared more than twenty years ago, has one of the highest ϕ angles for symmetrically out-of-plane bent alkenes ($\phi_{ex.} = 35.9°$).[7] Recent studies have revealed the unusual reactivity of this compound.[8] Even higher pyramidalization values were determined for bridgehead-substituted tribenzodihydroacepentalenes ($\phi_{ex.}$ = 45.8 and 47.2°),[9] however, these molecules are asymmetrically bent, i.e. the pyramidalization angles for the second olefinic carbon atom are much lower ($\phi_{ex.}$ = 27.6 and 30.2°). In the series of *isolable* unsaturated dodecahedrane molecules, for dodecahedradiene a remarkably high pyramidalization angle was calculated ($\phi_{calc.} = 42.9°$).[10][11] Recently, we discovered a simple reaction sequence which results in cage compounds with a twofold bridged sesquinorbornene structure.[12] We expected these compounds to exhibit an additional increase in double-bond nonplanarity compared with their unbridged analogues. Herein we describe synthetic improvements and studies on the chemical reactivity as well as theoretical investigations with these molecules.

Figure 1. Pyramidalization angle ϕ



A sequence of inter- and intramolecular Diels-Alder reactions of the dihydropentalene **1**[13] with 1 equivalent of *p*-benzoquinone gave the cage compound **2a** in relatively low yields (15−20%). The major product was the 1:2 adduct **3a** from **1** and two equivalents of *p*-benzoquinones. (Scheme 1).

Scheme 1

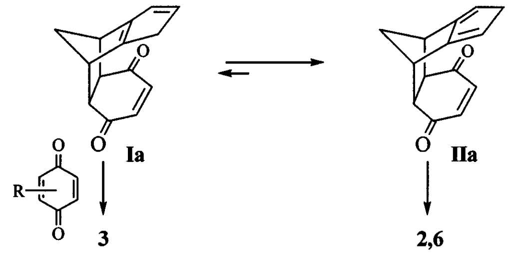


(i) 1 eq. benzoquinone, CH_2Cl_2, r.t., 24h

For other monofunctional dienophiles such as maleic anhydride, the equilibrium constant of the double-bond isomers **I** and **II** could be determined (ca. 5). This was not possible for the benzoquinone adducts **Ia** and **IIa** due to the rapid consumption of **IIa** by intramolecular cycloaddition. When the reaction of **1** and benzoquinone was performed with 0.2 equivalents of benzoquinone, the primary Diels-

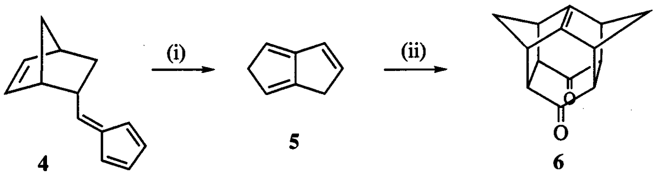
Alder cycloadduct **Ia** was detected by low-temperature ^{1}H NMR and the activation barrier for isomerization was determined to be 23 ± 2 kcal/mol (see Scheme 2).

Scheme 2



In order to improve the yield of cage compounds we examined two modifications: (a) Use of more reactive benzoquinones which should accelerate the intra- versus the intermolecular cycloaddition, and (b) application of the dilution principle in order to suppress the addition of a second equivalent of benzoquinone to the intermediate **I**. Treatment of the 1,5-dihydropentalene **1** with 2-(4-nitrophenyl)benzoquinone as bifunctional nonsymmetric dienophile resulted in two regioisomeric products **2b** and **2c** in a ratio of 57:43 (Scheme 1). The constitution of the cage products could be easily derived from the H-H coupling patterns. Surprisingly, no 1:2 cycloaddition products were isolated. As can be seen from the product substituent pattern, the primary cycloaddition exclusively involves the unsubstituted benzoquinone double bond (which can be easily derived from the H-H coupling pattern in the products). Thus, the secondary intramolecular cycloaddition must have been accelerated by the *p*-nitrophenyl group and the intermolecular reaction is widely suppressed. The second alternative was the use of dilution conditions. By slow addition of *p*-benzoquinone to a solution of **1** in dichloromethane the yield of **2a** could be raised to 52%. More important was the fact that this procedure allowed the preparation of the unsubstituted cage compound **6** from 1,5-dihydropentalene **5** (Scheme 3). The starting material **5** is easily available by thermolysis of the pentafulvene **4**.[14][15] After treatment with 1.1 equivalents of *p*-benzoquinone under dilution conditions, a 65:35 mixture of cage product **6** and a 1:2 cycloaddition product were isolated. After flash chromatography, **6** could be isolated as a colorless oil in 29% yield.

Scheme 3

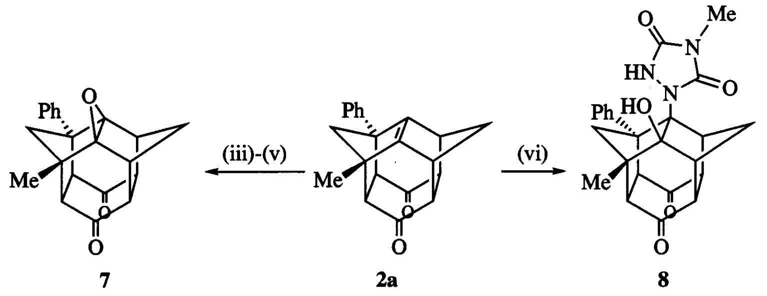


Unfortunately, no X-ray analysis could be performed so far, neither from the parent compound **6** nor from its derivatives **2** due to low crystal quality. Nevertheless, we tried to gain more information on the double-bond deformation by studying the chemical behaviour and performing calculations (vide infra). A characteristic property of *syn*-sesquinorbornenes is that they readily add oxygen to give the corresponding epoxides.[16] Actually, the cage compound **2a** was quantitatively epoxidized by a variety of reagents: Dimethyldioxirane (DMD) gave the epoxides **7** already after some minutes at −20 °C, singlet oxygen likewise reacted efficiently, whereas triplet oxygen needed some days for completion (Scheme 4). Oxirane **7** was crystallized as its methanol adduct and characterized by X-ray analysis.[17] It is important to mention, that no trace of 1,2-dioxetane or the corresponding cleavage products were formed in the singlet-oxygen reaction. Dioxetane formation can be found for many strained alkenes which have no properly aligned allylic hydrogen atoms.[18] Thus, the pyramidalization of the central double bond is depicted in a radical-like behaviour in its reaction with triplet oxygen as well as the unusual oxygen-atom transfer from singlet oxygen. That this behaviour is not a consequence of extreme shielding by the two flanking methylene bridges became apparent from the reaction of **2a** with *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) in aqueous THF which led to the adduct **8**. For TAD [2 + 2] cycloaddition reactions an intermediate aziridinium imide zwitterion has been proven recently.[19] Thus, adduct **8** probably resulted from the nucleophilic ring opening of such an intermediate with substrate **2a**.

In order to gain more detailed information on the degree of double-bond deformation, we performed a series of semiempirical and DFT calculations for the unsubstituted cage compound **6**, its deoxygenated (hypothetical) analogue **9** (in order to exclude through-space carbonyl-carbonyl interactions) and the tetradehydrodianthracene **10** (Figure 2). Force field calculations (MM2[20]) resulted in too high values for the pyramidalization angle ϕ: e.g. for Greene's compound **10** a ϕ value of 43.3° resulted ($\phi_{ex.}$ = 35.9°). Semiempirical methods resulted in more realistic values: AM1[21] calculation gave 35.4° for **10** [for C_{60} $\phi_{calc.}$ is 31.9° ($\phi_{ex.}$ = 31.6°)]. For compound **6** the force field predicts a pyramidalization of 52.8°, the AM1 calculation gave 48.6°. To further optimize these results we performed density functional theory calculations (DFT-B3LYP[22]) with the 6-31G* basis set.[23] The GAUSSIAN94 program package was used for these calculations.[24] The results for **6** and **9** were nearly identical: for **6** a ϕ value of 46.5° (**9**: 47.1°) resulted (Table 1). Another useful parameter for the description of large symmetrical out-of-plane bending is the α_{av} value.[25][26][28] For Greene's compound **10** α_{av} is 114.8°, for C_{60} a_{av} = 116° (from X-ray data). The DFT calculations for **6** and **9** resulted in α_{av} values of 114.4° and 114.2°, respectively. These calculations lead to the suggestion that the (at room temperature stable) cage compounds **2**, **6** have remarkably high double-bond pyramidalizations. This pyramidalization results mainly from the fact that the strong compression of the α and β angles, which is typical for sesquinorbornenes, cannot be counterbalanced by expansion of the γ angle. In typical *syn*-sesquinorbornenes the γ angle can reach values up to 144°.[3a]

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB 347, University of Würzburg) and the *Fonds der Chemischen Industrie.*

Scheme 4

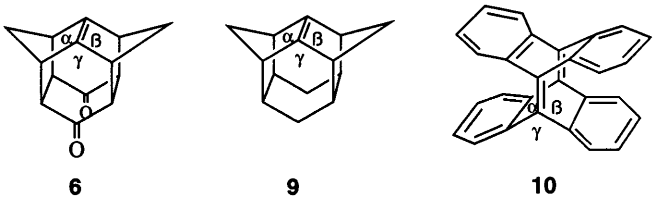


(iii) DMD, acetone, -30°C, 10 min; (iv) CH_2Cl_2, TPP, O_2, -10°C; (v) CH_2Cl_2, O_2, r.t., 5d; (vi) MTAD, THF-H_2O, -20°C, 1h.

Table 1. Results of calculations for **6** (**9**)

	MM2	AM1	B3LYP/6-31G*
α	107.25	106.77	107.62 (107.55)
β	107.25	106.77	107.62 (107.55)
γ	121.23	128.18	127.87 (127.53)
$\alpha + \beta + \gamma$	335.73	341.72	343.11 (342.63)
ϕ	52.8	48.6	46.5 (47.1)
$\alpha_{av.}$	111.91	113.91	114.37 (114.21)

Figure 2. Pyramidalized alkenes **6**, **9**, **10**



Experimental Section

General: The dihydropentalenes **1** and **5** were synthesized according to literature procedures.[13][14] – IR: Perkin-Elmer 1420. – ^1H NMR: AC 200 (200 MHz), Bruker AC 250 (250 MHz), Bruker AC 300 (300 MHz) Bruker AC 500 (500 MHz). – ^{13}C NMR: Bruker AC 200 (50.3 MHz), Bruker AC 250 (63.4 MHz), carbon multiplicities were determined by DEPT. – For ^1H NMR, $CDCl_3$ as solvent, TMS as internal standard; for ^{13}C NMR, $CDCl_3$ (δ_C = 77.0). – Column chromatography: Silica gel (Merck) 60–230 mesh; petroleum ether (PE, 40–60°C), ethyl acetate (EA). – Combustion analyses: Institut für Anorganische Chemie der Universität Würzburg.

1-Methyl-8-phenyl-hexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**2a**): A solution of 1.95 g (18.0 mmol) of *p*-benzoquinone in 100 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 3.50 g (18.0 mmol) of **1** in 1000 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, column chromatography (CH_2Cl_2/EA, 5:1, R_f = 0.45) resulted in 2.83 g (52%) of **2a** as a colorless powder, m.p. 108–109°C (ref.[12] 106–108°C).

1-Methyl-5-(4-nitrophenyl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**2b**) *and 1-Methyl-4-(4-nitrophenyl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione* (**2c**): A solution of 2.60 g (11.3 mmol) of 2-(4-nitro-phenyl)benzoquinone in 150 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 2.20 g (11.3 mmol) of **1** in 600 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, column chromatography resulted in 1.90 g (40%) of a mixture of **2b** and **2c** as a brown solid which was recrystallized several times from cyclohexane to give 1.20 g (25%) of a 1.3:1 mixture of **2b** and **2c** as a colorless powder. – IR (CCl_4, mixture): $\tilde{\nu}$ = 3010 cm^{-1}, 2940, 1695, 1590, 1510, 1340, 1250, 1130. – **2b**: ^1H NMR ($CDCl_3$): δ = 1.55 (s, 3H), 1.73 (d, J = 10.1 Hz, 1 H, 11-H_{anti}), 1.93 (d, J = 10.3 Hz, 1 H, 14-H_{anti}), 2.19 (m, 2 H, 11-H_{syn}, 14-H_{syn}), 2.96 (dd, J = 2.9, 8.0 Hz, 1 H, 2-H), 3.08 (dd, J = 2.9, 3.5 Hz, 1 H, 4-H), 3.52 (d, J = 8.0 Hz, 1 H, 7-H), 3.65 (m, 1 H, 12-H), 4.03 (s, 1 H, 10-H), 7.20–7.51 (m, 7 H, Ar.-H), 8.10–8.20 (m, 2 H, Ar.-H). – ^{13}C NMR ($CDCl_3$): δ = 15.1 (q), 41.8 (t), 51.5 (d), 55.0 (d), 56.2 (t), 60.2 (s), 62.4 (d), 65.4 (d), 65.6 (d), 68.8 (s), 70.0 (s), 123.3 (d), 127.3 (d), 127.6 (d), 128.8 (d), 129.7 (d), 136.4 (s), 137.2 (s), 146.7 (s), 157.7 (s), 160.3 (s), 208.5 (s), 209.4 (s). – **2c**: ^1H NMR ($CDCl_3$): δ = 1.54 (s, 3H), 1.75 (d, J = 10.6 Hz, 1 H, 11-H), 1.94 (d, J = 10.3 Hz, 1 H, 14-H), 2.19 (m, 2 H, 11′-H, 14′-H), 3.01 (d, J = 8.0 Hz, 1 H, 2-H), 3.02 (dd, J = 2.8, 3.6 Hz, 1 H, 5-H), 3.46 (dd, J = 2.8, 8.0 Hz, 1 H, 7-H), 3.65 (m, 1 H, 10-H), 4.03 (s, 1 H, 12-H), 7.20–7.51 (m, 7 H, Ar.-H), 8.10–8.20 (m, 2 H, Ar.-H). – ^{13}C NMR ($CDCl_3$): δ = 15.1 (q), 41.8 (t), 52.2 (d), 54.0 (d), 55.9 (t), 60.7 (s), 63.2 (d), 65.1 (d), 65.2 (d), 68.3 (s), 69.6 (s), 123.4 (d), 127.3 (d), 127.6 (d), 128.8 (d), 129.7 (d), 136.4 (s), 137.2 (s), 147.0 (s), 154.8 (s), 157.4 (s), 208.5 (s), 209.4 (s).

Hexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**6**): A solution of 1.36 g (12.65 mmol) of *p*-benzoquinone in 100 ml of CH_2Cl_2 was added under nitrogen at room temp. to a solution of 1.20 g (11.5 mmol) of **5** in 1000 ml of CH_2Cl_2 by means of a motor-driven syringe during 24 h. After evaporation of the solvent, flash chromatography resulted in 0.71 g (29%) of **6** as a colorless oil. – IR (CCl_4): $\tilde{\nu}$ = 2975 cm^{-1}, 1725, 1685, 1265, 1090. – ^1H NMR ($CDCl_3$): δ = 1.35 (d, J = 10.2 Hz, 2 H, 11-H_{anti}, 14-H_{anti}), 1.84 (d, J = 10.2 Hz, 2 H, 11-H_{syn}, 14-H_{syn}), 2.64 (s, 4H), 3.35 (s, 4H). – ^{13}C NMR ($CDCl_3$): δ = 42.3 (t, C-11, C-14), 52.3 (d, 4C), 56.6 (d, 4C), 154.9 (s, C-9, C-13), 211.7 (s, 2 C=O). – $C_{14}H_{12}O_2$ (212.2): calcd. C 79.21, H 5.70; found C 79.40, H 5.64.

1-Methyl-8-phenyl-9,13-epoxyhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradeca-3,6-dione (**7**): A solution of 80 mg (0.27 mmol) of compound **2a** in 2 ml of CH_2Cl_2 and 1 mg of tetraphenylporphine (TPP) was irradiated with a 150-W sodium lamp at −10°C under constant purging with dry oxygen (syringe needle). After evaporation of the solvent, the residue was chromatographed which resulted in 60 mg (71%) of colorless needles, m. p. 115–117°C. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 2920, 1700, 1680, 1425, 1255. – ^1H NMR ($CDCl_3$): δ = 1.33 (dd, J = 1.3, 10.7 Hz, 1 H, 11-H_{anti}), 1.39

(s, 3H), 1.55 (d, J = 10.7 Hz, 1 H, 14-H$_{anti}$), 2.19 (dd, J = 1.6, 10.7 Hz, 1 H, 11-H$_{syn}$), 2.36 (d, J = 10.7 Hz, 1 H, 14-H$_{syn}$), 2.93 (dd, 1 H, J = 2.8, 9.7 Hz, 1 H, 2-H), 3.02 (m, 2 H, 4-H, 5-H), 3.21 (m, 2 H, 10-H, 12-H), 3.43 (dd, J = 2.8, 9.7 Hz, 1 H, 7-H), 7.28−7.42 (m, 5 H, Ph.-H). − ^{13}C NMR (CDCl$_3$): δ = 14.6 (q), 37.4 (t), 45.6 (d), 45.9 (d), 51.3 (t), 53.9 (s), 57.2 (d), 57.6 (d), 60.8 (s), 62.1 (s), 62.2 (d), 62.9 (s), 64.7 (d), 126.6 (d), 127.6 (d), 128.8 (d), 137.0 (s), 208.3 (s), 208.4 (s). − $C_{21}H_{18}O_3$ (318.4): calcd. C 79.20, H 5.70; found C 78.67, H 5.60. − Crystallization of the crude material from methanol resulted in a methanol addition product in 96% yield.[17]

13-Hydroxy-1-methyl-9-(4-methyl-3,5-dioxo-1,2,4-triazolin-1-yl)-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (**8**): A solution of 1.00 g (3.3 mmol) of **2a** in 100 ml of aqeous THF was precooled to −20°C and a solution of 0.38 g (3.3 mmol) of MTAD in 20 ml of THF was added within 10 min. After stirring for 16 h at room temperature, the solvent was evaporated and the residue dissolved in 5 ml of acetone. After cooling to −10°C, 0.48 g (35%) of **8** crystallized as colorless needles m.p. 279−280°C. − IR (CCl$_4$): $\tilde{\nu}$ = 3280 cm^{-1}, 2920, 1735, 1670, 1090, 1070. − ^{1}H NMR (CDCl$_3$): δ = 0.72 (s, 3H), 1.39 (d, J = 11.0 Hz, 1 H, 11-H$_{anti}$), 1.49 (d, J = 11.3 Hz, 1 H, 14-H$_{anti}$), 2.31 (d, J = 12.2 Hz, 1 H, 2-H), 2.46 (d, J = 12.2 Hz, 1 H, 7-H), 2.50 (mc, 1 H, 11-H$_{syn}$), 2.56 (s, 2 H, 4-H, 5-H), 2.63 (s, 3 H), 2.70 (s, 1 H, 12-H), 3.18 (d, J = 11.3 Hz, 1 H, 14-H$_{syn}$), 4.69 (s, 1 H, 10-H), 5.72 (s, 1 H, OH), 6.72−6.96 (m, 5 H, Ph.-H), 8.44 (s, 1 H, NH). − ^{13}C NMR (CDCl$_3$): δ = 15.9 (q), 24.7 (q), 43.3 (t), 50.3 (d), 52.3 (d), 52.7 (d), 53.5 (d), 54.2 (t), 57.4 (s), 57.8 (d), 60.0 (d), 63.9 (s), 80.1 (s), 91.3 (s), 126.9 (d), 127.6 (d), 128.0 (d), 138.3 (s), 153.3 (s), 153.4 (s), 208.5 (s), 210.7 (s). − $C_{24}H_{23}N_3O_4$ (417.5): calcd. C 69.05, N 10.07, H 5.55; found C 68.93, N 9.93, H 5.70.

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