

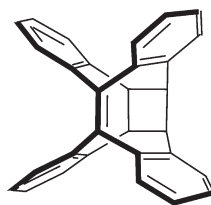
Cage Hydrocarbons Derived from Dibenzosuberone

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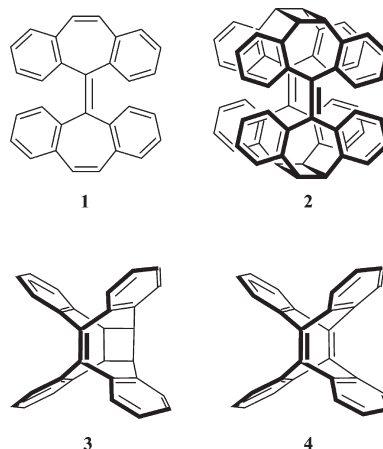
The reinvestigation of the synthesis of the fascinating cage compound **2** reveals an incorrect structure of photodimer **2**, as well as of the putatively isolated intermediate **9**. These products have to be reassigned as monomeric pyramidalized alkene **3** and spirocyclic dichloride **10**, respectively.

Introduction

The [2+2]-photocyclization is a common key step in the synthesis of caged hydrocarbons with considerable ring strain.¹ Forty years ago Praefcke et al.² described the photodimerization of tetrabenzoheptafulvalene **1** to the fascinating belt-like³ hydrocarbon **2**, which should be of interest for the construction of unusual carbon nanotubes⁴ or spherical hydrocarbons¹ with four- and seven-membered rings.

However, we had doubts about structure **2** for several reasons. First, it is not obvious why photodimerization of **1** should favor the endo over the exo dimer, the logical precursor to **2** (Scheme 1). Second, our semiempirical PM3 calculations show that **2** is more strained than two molecules of **3** by 73 kcal/mol. Third, the photocyclization of bisuberenyl ether and amine⁵ proceeds in intramolecular fashion,

SCHEME 1. Tetrabenzoheptafulvalene **1** with Related Cage Compounds



giving products analogous to **3**.⁶ Fourth, the only proof of structure **2** was an osmometric determination of the molecular mass to be about 800 to 900 g/mol, seemingly ruling out the monomeric photocyclization product **3**. On the basis of these concerns, we decided to reinvestigate the photocyclization of **1**. Moreover we became interested in monomer **3**, because of its obvious structural similarity to dehydrobisanthracene **4**, which has been extensively studied by Herges⁷ because of its synthetic potential for the construction of hydrocarbon picotubes and Möbius annulenes.

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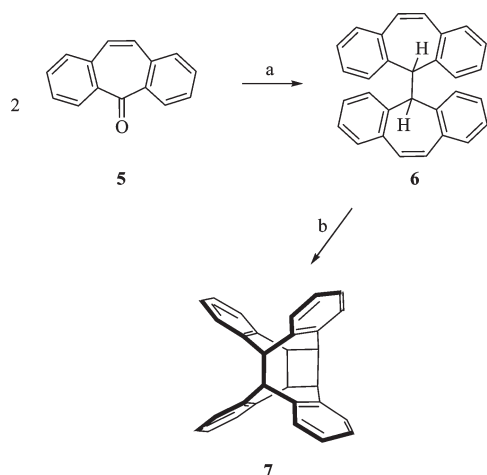
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SCHEME 2. Synthesis of Cage Compound 7^a

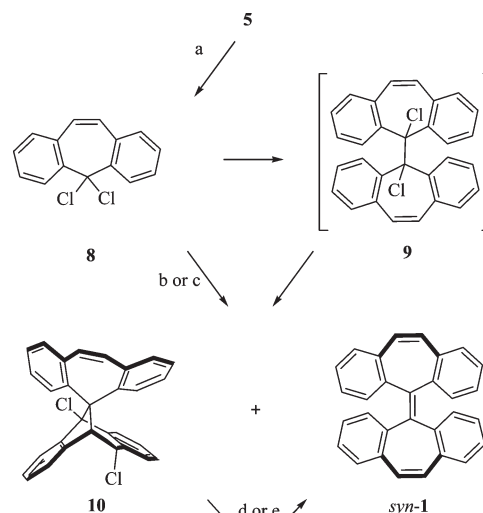
^aReagents and conditions: (a) TiCl_4 , Zn, THF, screw-capped tube, 6 h, 100 °C, 36%; (b) *hν*, xylene, 48 h, 65%.

Results/Discussion

We tried to improve the reported synthesis of tetrabenzoheptafulvalene **1**⁸ by applying Fürstner's "instant McMurry" procedure on dibenzosuberone **5**,⁹ but we isolated exclusively the hydrogenated compound **6**.^{10,11} Compound **6** is an interesting model substrate for the photocyclization (Scheme 2): irradiation in xylene smoothly led to the formation of cage compound **7**, which was fully characterized by spectroscopic means and was additionally identified by X-ray crystal structure analysis (Figure 2).¹²

For the synthesis of **1** we then decided to follow the procedure of Bergmann,¹³ who transformed the geminal dichloride **8**¹⁴ by a bronze induced Ullmann coupling reaction¹⁵ and reported to have isolated the vicinal dichloride **9** as intermediary product (Scheme 3). In our hands the product distribution was clearly influenced by the activity of the copper bronze: before use the copper bronze (90% Cu, 10% Sn, 100 mesh) was first activated with iodine/acetone, then with HCl/acetone,¹⁶ washed with acetone, and dried in vacuo for 1 h in the Kugelrohr oven, either at 100 °C giving higher activity bronze, or at 250 °C yielding the less active bronze (presumably because of sintering processes at the surface).

With the less active bronze in toluene at reflux temperature we obtained the spirocyclic dichloride **10** (Figure 1) as the main product instead of the vicinal dichloride **9** reported in the

SCHEME 3. Intermediates in the Synthesis of *syn*-**1**^a

^aReagents and conditions: (a) PCl_5 , POCl_3 , 3 h, 120 °C, **8** was not isolated; (b) less active Cu bronze, toluene, 7 h, reflux, 40% of **10** and 24% of *syn*-**1**; (c) higher active Cu bronze, toluene, 7 h, reflux, 7% of **10** and 36% of *syn*-**1**; (d) higher activity Cu bronze, toluene, 7 h, reflux, 93% of *syn*-**1**; (e) 10% $\text{Pd}(\text{OAc})_2$, K_2CO_3 , *n*- $\text{Bu}_4\text{N}_4\text{Br}$, DMF, 3 d, 140 °C, 98% of *syn*-**1**.

literature.² In the ¹H NMR spectrum of compound **10** the characteristic 2H AB-signal of the two vicinal benzylic protons is registered at 4.71 and 4.90 ppm with $J = 4.8$ Hz. The X-ray structure analysis clarified the configuration of the diastereoisomer, with the *mono*-benzylic chloride in the *trans*-position to the *spiro*-carbon atom. Presumably the reports on the vicinal dichloride **9** are simply incorrect, since the reported melting point of 250 °C for **9** is close to the 260 °C we found for **10**. Mechanistically **10** of course should derive from **9** via a three-step process consisting of ion dissociation (chloride and dibenzotropylium cation), transannular cyclization, and C–Cl-bond formation at benzylic cation.

Higher activity bronze led to increased formation of our target molecule *syn*-**1**, the preferred conformer as reported earlier in the literature. Most interestingly the spirocyclization can be reversed: both with higher activity copper bronze

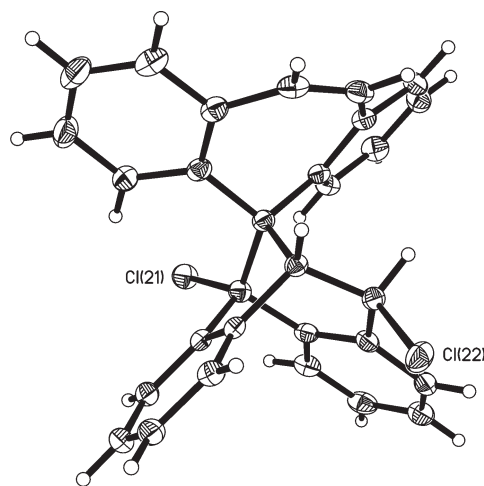


FIGURE 1. Structure of spirocycle **10** in the crystal.¹²

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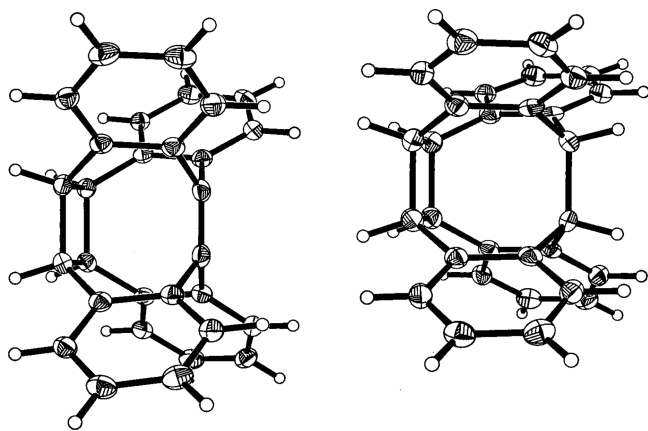


FIGURE 2. Structures of the cage compounds **3** and **7** in the crystal.¹²

and also under palladium catalysis the transformation to the desired *syn-1* succeeds almost quantitatively.

Triene *syn-1* was irradiated in toluene, highly diluted (0.0013 molar), and also highly concentrated (0.049 M): in both cases exclusively the monomeric intramolecular photocyclization product **3** was isolated in good to excellent yield. The structure of **3** (Figure 2) in the crystal appears slightly twisted; therefore two different pyramidalization angles¹⁷ 19.6° and 19.8° were found (moderate compared to the 35° of tetrahydrodianthracene **4**¹⁸). Even by mass spectroscopy of the crude product we could not find any hint of the formation of dimer **2**. Since the reported melting point of 327 °C for **2** is close to the 335 °C we found for **3**, we assume that the reported identification² of compound **2** based on osmolytic molecular mass determination was incorrect.

In conclusion, we have presented a short and efficient synthesis of the pyramidalized alkene **3**, which seems to have been erroneously identified as photodimer **2** 40 years ago. The synthesis of dimer **2** is still an unsolved problem in synthesis. Future work will concentrate on the dimerization of **3** as entry to **2**, in analogy of the successful cycloaddition/cycloreversion sequence of didehydrodianthracene **4** as demonstrated by Herges.¹⁹

Experimental Section

Titan-Induced Coupling Reaction of Dibenzosuberone (5). A sample of 540 mg (2.62 mmol) of dibenzosuberone (**5**), 519 mg (2.74 mmol) of titanium tetrachloride, and 436 mg (6.67 mmol) of zinc powder in 50 mL of dry THF in a screw-capped tube was stirred under argon for 6 h at 100 °C. After adsorptive filtration through a pad of silica (3 g) with ethyl acetate as additional eluent and after concentrating to dryness the residual starting material was removed by sublimation at 75 °C and 0.6 mbar in a Kugelrohr oven. The crude product was recrystallized from CH₂Cl₂/MeOH to yield 181 mg (36%) of 5*H*,5'*H*-[5,5']bi[dibenzo[*a*,*a'*]cycloheptenyl] (**6**) as colorless crystals with mp 324 °C (in the literature the reported melting point varies from 295 °C¹⁹ to 327 °C^{2b}). ¹H NMR (400 MHz, CDCl₃) δ 4.73 (s,

2 H), 6.62 (“dd”, *J* = 7.6, 1.0 Hz, 4 H), 6.89 (dt, *J* = 7.6, 1.5 Hz, 4 H), 7.01 (dt, *J* = 7.6, 1.3 Hz, 4 H), 7.06 (s, 4 H), 7.23 (“dd”, *J* = 7.6, 1.3 Hz, 4 H) ppm. MS (EI, 70 eV) *m/z* (%) 382 (1.9) [M⁺], 191 (100), 165 (19).

Intramolecular [2+2]-Photocycloaddition of 6. A suspension of 100 mg (26 mmol) of **6** in 200 mL of xylene was degassed with argon for 30 min prior to irradiation with a 125 W Hg vapor lamp for 48 h. After evaporation of the solvent (75 °C, 0.6 mbar) the residue was purified by flash chromatography (20 g silica gel, petroleum ether/dichloromethane 5:1; *R_f* 0.17) and the product was dried in vacuo (75 °C, 0.5 mbar, 120 min): 65 mg (65%) of cage compound **7** as colorless crystals with mp 313 °C. IR (KBr) $\tilde{\nu}$ 3058 (w), 3020 (w), 2926 (w), 1492 (m), 1448 (m), 762 (s), 627 (s), 605 (m), 537 (w) cm⁻¹. UV (acetonitrile) λ_{\max} (log ϵ) 264 (3.19), 220 (4.22) nm. ¹H NMR (600 MHz, CDCl₃) δ 4.58 (s, 4H), 4.79 (s, 2H), 6.79 (“t”, *J* = 4.5 Hz, 4H), 6.91 (m, 8H), 7.05 (“t”, *J* = 4.5 Hz, 4H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 46.8 (d), 58.9 (d), 127.1 (d), 127.3 (d), 130.44(d), 131.43 (d), 137.6 (s), 141.7 (s) ppm. MS (EI, 70 eV) *m/z* (%) 382 (12) [M⁺], 204 (31), 191 (100), 178 (18), 165 (5). HR-MS (EI, 70 eV) calcd for C₃₀H₂₂ 382.17215 [M⁺], obsd 382.16803.

Activation of Copper Bronze.¹⁶ Copper bronze (100 g, 99%, 100 mesh from Alfa-Aesar) was subsequently treated with 1000 mL of a solution of iodine (2% weight) in acetone for 5–10 min, after filtration with 500 mL of concentrated HCl in acetone (1:1, v/v), and washed three times with 150 mL of acetone. With drying for 1 h in a Kugelrohr oven at 250 °C 82 g of less active copper bronze was obtained, while drying at 100 °C gave copper bronze of significantly higher activity.

1,4-Dichloro-2,3–5,6-dibenzospiro[bicyclo[3.2.1]octane-8,1'-dibenzosuberone] (10) and syn-2,3,6,7,2',3',6',7'-Tetrabenzoheptafulvalen (syn-1). A mixture of 1.65 g (8 mmol) of ketone **5**, 1.66 g (8.0 mmol) of PCl₅, and 8 mL of POCl₃ in a 250 mL round-bottomed flask fitted with a reflux condenser was heated under argon for 3 h at 130 °C. POCl₃ was distilled off under reduced pressure. To the crude residual dichloride **8** were added 3.30 g of copper bronze and 25 mL of dry toluene and the mixture was stirred at 115 °C for 7 h. The reaction mixture was treated with 50 mL of brine and with 50 mL of methyl *tert*-butyl ether and the aqueous layer was extracted twice with 40 mL of methyl *tert*-butyl ether. The combined organic layer was dried over sodium sulfate and concentrated. The residue was fractionated by flash chromatography (silica, petroleum ether/dichloromethane 5:1) giving various amounts of spirodichloride **10** and heptafulvalen *syn-1* depending on the activity of the copper bronze applied; less active copper bronze gave 730 mg (40%) of **10** and 105 mg (7%) of *syn-1*, while copper bronze of higher activity yielded 428 mg (24%) of **10** and 455 mg (36%) of *syn-1*. Physical and spectroscopic data of the isolated compounds follow. **Spirodichloride 10:** colorless crystals with mp 260 °C. IR (KBr) $\tilde{\nu}$ 3065 (w), 3052 (w), 3018 (w), 1472 (w), 922 (w), 795 (m), 765 (m), 743 (w), 733 (w), 716 (m), 700 (w), 629 (m), 610 (w), 504 (w), 469 (m), 449 (s) 440 (m), 429 (m), 416 (s) cm⁻¹. UV (acetonitrile) λ_{\max} (log ϵ) 236 (4.03), 295 (3.96) nm. ¹H NMR (400 MHz, CDCl₃) δ 4.71 (d, *J* = 4.8 Hz, 1 H), 4.90 (d, *J* = 5.1 Hz, 1 H), 7.03 (“t”, *J* = 7.1, 1.5 Hz, 1 H), 7.09 (“t”, *J* = 7.3, 0.8 Hz, 1 H), 7.13 (d, *J* = 7.1 Hz, 1 H), 7.13–7.20 (m, 5H), 7.26 (“t”, *J* = 7.5, 1.5 Hz, 3 H), 7.29–7.34 (m, 1 H), 7.34–7.39 (m, 2 H), 7.63 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.48–8.54 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 51.73 (d), 57.4 (d), 71.2 (s), 82.2 (s), 120.2 (d), 123.5 (d), 125.9 (d), 126.6 (d), 127.6 (d), 127.72 (d), 127.75 (d), 128.1 (d), 128.31 (d), 128.31 (d), 128.5 (d), 128.6 (d), 129.1 (d), 130.6 (d), 130.7 (d), 131.1 (d), 131.2 (d), 131.5 (s), 134.1 (s), 134.2 (d), 134.3 (s), 134.8 (s), 135.6 (s), 141.5 (s), 143.4 (s), 149.3 (s) ppm. MS (EI, 70 eV) *m/z* (%) 450/452/454 (60/38/11) [M⁺], 415/417 (25/12) [M⁺ – Cl⁻], 380 (67) [M⁺ – 2Cl⁻], 363 (17), 350 (8), 302 (18), 272 (7), 225 (15), 212 (33), 202 (62), 191 (100), 178 (31), 152 (8), 117 (6), 91 (6), 84

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(14), 73 (35), 59 (30), 43 (29), 28 (15). Elemental analysis calcd for $C_{30}H_{20}Cl_2$ (451.39 g/mol): C 79.83, H 4.47. Found: C 79.71, H 4.45. **Heptafulvalene *syn-1***: colorless crystals with mp 255 °C (according to literature² *syn-1* has mp 255 °C, whereas mp 332 °C is reported for *trans-1*). ¹H NMR (200 MHz, CDCl₃) δ 6.71 (s, 4H), 6.96–7.23 (m, 12 H), 7.55 (d, *J* = 7.3 Hz, 4 H) ppm. MS (EI, 70 eV) *m/z* (%) 380 (15) [M⁺], 240 (47), 202 (6), 169 (7), 149 (7), 119 (29), 93 (54), 84 (83), 57 (23), 49 (100).

Transformation of Spirodichloride 10 into Heptafulvalene *syn-1*. **Method A:** A mixture of 700 mg (1.55 mmol) of spirodichloride **10**, 1.5 g (31 mmol) of the higher active copper bronze, and 25 mL of dry toluene was heated under stirring at 115 °C for 7 h. After filtration and washing of the solid layer with methyl *tert*-butyl ether the liquid phase was concentrated and the residue recrystallized from methanol/dichloromethane (3:1) to give 550 mg (93%) of *syn-1* colorless crystals with mp 255 °C. **Method B:** A mixture of 226 mg (510 μmol) of spirodichloride **10**, 1.11 g (8.05 mmol) of dry potassium carbonate, 645 mg (2.00 mmol) of tetra-*n*-butyl ammonium bromide, and 12 mg (54 μmol) of palladium acetate in 10 mL of dry DMF in a screw-capped tube was heated under stirring at 140 °C for 3 d. After the addition of 50 mL of water, the layers were separated and the aqueous layer was extracted three times with 50 mL of diethyl ether. The combined organic layer was filtered through a pad of 3 g of silica and concentrated to dryness (75 °C, 1 mbar). The residue was recrystallized from methanol/dichloromethane (3:1) to give 190 mg (98%) of *syn-1* as colorless crystals with mp 255 °C.

Intramolecular [2+2]-Photocycloaddition of *syn-1*. A suspension of 102 mg (26 mmol) of *syn-1* in 200 mL of toluene was degassed with argon for 30 min prior to irradiation with a 125 W Hg vapor lamp for 12 h. After evaporation to dryness (75 °C, 0.6 mbar) the brownish residue was purified by recrystallization from methanol/dichloromethane and the resulting crystals, suitable for X-ray crystal structure analysis, were dried in vacuo (75 °C, 0.5 mbar, 120 min): 87 mg (85%) of cage compound **3** as colorless crystals with mp 335 °C (starting from 500 mg (1.31 mmol) of *syn-1* in 27 mL of toluene and 322 mg (64%) of **3**) was obtained. IR (KBr) $\tilde{\nu}$ 3059 (w), 3009 (w), 2943 (w), 1478 (m), 1448 (w), 757 (s), 713 (w), 635 (m), 610 (w) cm⁻¹. UV (acetonitrile) λ_{max} (log ϵ) 226 (3.97), 267 (3.16), 276 (3.13) nm. ¹H NMR (400 MHz, CDCl₃) δ 4.60 (s, 4H), 6.85 (“d”, *J* = 7.3, 1.0 Hz, 4H), 6.95 (“t”, *J* = 7.6, 1.5 Hz, 4H), 7.02 (“t”, *J* = 6.6, 1.3 Hz, 4H), 7.21 (“d”, *J* = 7.6, 1.3 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 49.3 (d), 124.9 (d), 127.3 (d), 127.4 (d), 130.2 (d), 136.9 (s), 143.1 (s), 144.9 (s) ppm. MS (EI, 70 eV) *m/z* (%) 380 (84) [M⁺], 363 (11), 350 (5), 302 (8), 240 (100), 221 (37), 206 (42), 190 (17), 178 (27), 149 (30), 129 (5), 120 (45), 93 (100), 77 (62), 66 (17), 57 (14), 44 (63). HR-MS (EI, 70 eV) calcd for C₃₀H₂₀ 380.15649 [M⁺], obsd 380.15591.

Supporting Information Available: General experimental methods, proton NMR spectra of new compounds, and crystallographic information files for **3**, **7**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.