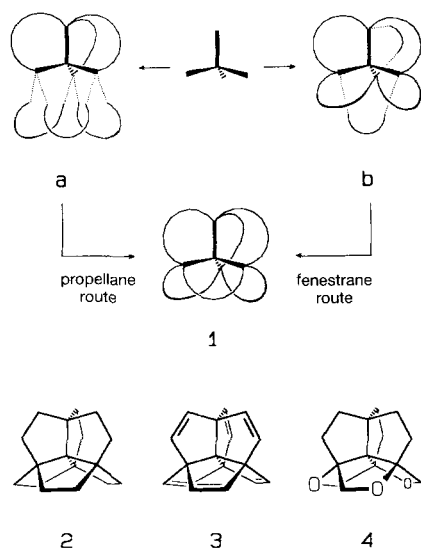


# Synthesis of Centrohexasicyclic Hydrocarbons by the Propellane Route: Centrohexasindan and Tribenzocentrohexasquinane\*\*

Dietmar Kuck,\* Bernd Paisdor, and Detlef Gestmann

Dedicated to Dr. Howard E. Simmons, Jr.  
on the occasion of his 65th birthday

The construction of centrohexasicyclic hydrocarbon frameworks with the general structure **1** (centrohexasicyclanes;<sup>[1]</sup> Scheme 1) continues to present a challenge in organic polycycle chemistry. In these types of structures six annelated carbocycles share a central neopentane unit of five quaternary carbon atoms and form a microlattice with nonplanar topology.<sup>[2]</sup> The compounds with six centrally annelated cyclopentane rings should be relatively strain-free.<sup>[1, 3]</sup> Thus relatively undistorted frameworks of, for example, perhydrotriquinacene and all-*cis*-[5.5.5]fenestrane can be found in the yet unknown parent structure, centrohexasquinane **2**, which can be considered to be the condensation center of four pentagon dodecahedrane units.<sup>[1]</sup> Nevertheless, synthetic routes to **2** and centrohexasquinacene **3**, which was first

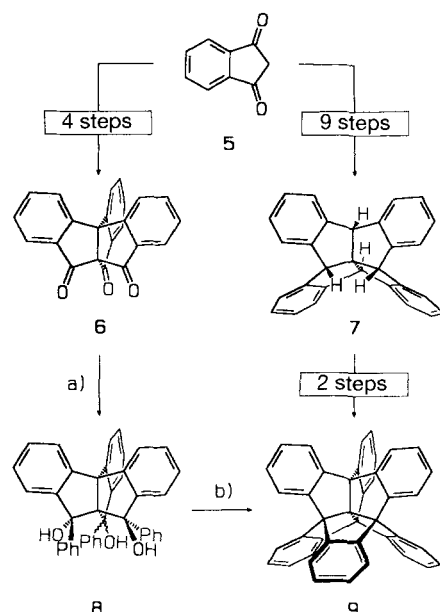


Scheme 1.

proposed in 1978,<sup>[4]</sup> must take into account considerable steric compression and/or fragmentation between the components that are to be joined. Therefore, not surprisingly, centrohexasicyclic hydrocarbons<sup>[5, 6]</sup> and the corresponding heterocycles<sup>[7–9]</sup> have remained quite rare. Only one directed synthesis of a centrohexasicyclic hydrocarbon framework was reported previously, namely the synthesis of the sixfold benzoannelated derivative of **2**, centrohexasindan **9**.<sup>[5]</sup> We have now discovered a new route to **9** and centrohexasicyclic triethers related to the "Simmons–Paquette molecule" **4**<sup>[8, 9]</sup> and have developed a synthesis of the novel tribenzocentrohexasquinanes.

In our first synthesis of **9** the already highly condensed fenestrindan **7**, which is thus protected against fragmentation, was

bridged twice (route **b** to **1** in Scheme 1 and route **5** → **7** → **9** in Scheme 2). A newer alternative synthesis, the propellane route, starts with 9,10,11-triptyndantrione **6**,<sup>[10]</sup> a [3.3.3]propellane accessible from 1,3-indandione **5** in only four steps (route **a** to **1** in Scheme 1 and route **5** → **6** → **8** → **9** in Scheme 2).



Scheme 2. Synthesis of centrohexasindan **9** by the propellane route and by the fenestrane route. **5** → **6**: ref. [10]; **5** → **9**: ref. [5]. a) PhLi (20 mol) in benzene/Et<sub>2</sub>O/*c*-C<sub>6</sub>H<sub>12</sub>; H<sub>2</sub>O; b) H<sub>3</sub>PO<sub>4</sub>/xylene, Δ; yield 40% of **6**.

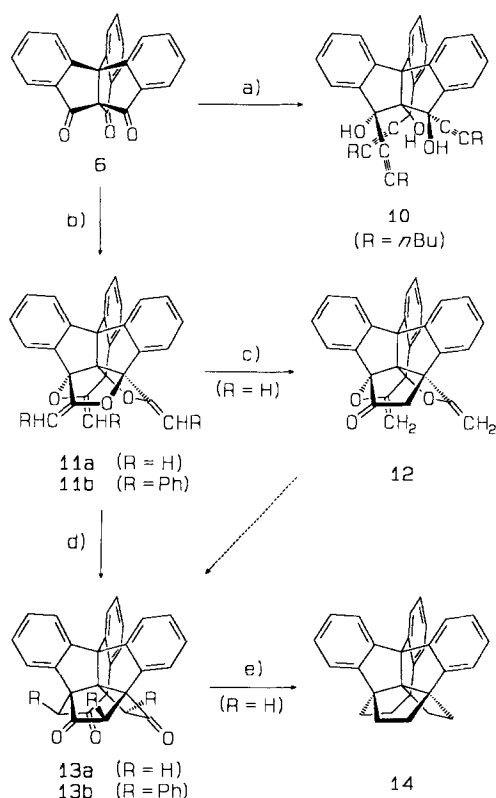
Three equivalents of aliphatic Grignard compounds like CH<sub>3</sub>MgBr and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>MgBr can be added to triptyndantrione **6** with remarkable ease and without ring opening. Only two equivalents of phenylmagnesium bromide react with **6**,<sup>[10]</sup> however, threefold addition is possible if phenyllithium is employed in a poorly solvating medium. After hydrolysis a mixture of isomeric triols **8** is obtained, which can be cyclodehydrated with acid catalysis to give **9**. These two steps, in which a total of six C–C bonds are formed, conclude the synthesis of centrohexasindan **9** from **5** in only six steps and with a total yield of up to 24%.<sup>[11]</sup>

The propellane route was then used for the first construction of centrohexasquinanes with *partial* benzoannelation. The synthesis of tribenzocentrohexasquinane **14** is shown in Scheme 3. In this synthesis a C<sub>2</sub> synthon was required which, in analogy to the sequence **6** → **8** → **9**, would undergo threefold nucleophilic addition to **6** and subsequent cyclization to yield the triquinacene framework complementary to the [3.3.3]propellane unit. Neither the application of the strategies used by Simmons III and Maggio,<sup>[8]</sup> and by Paquette et al.<sup>[9]</sup> (e.g. rearrangement of a trispiro[[3.3.3]propellanetriss(oxirane)]) to **4** to the triptyndantrione system nor other approaches of our own were successful.<sup>[10, 12, 13]</sup> A surprisingly direct route to **14** and interesting derivatives is based on the threefold reaction of **6** with lithium acetylides.

Unexpectedly, the reaction of triptyndantrione **6** with three equivalents of lithium acetylide in THF furnishes not triol **10** (R = H) but tris(enol ether) **11 a**, the first derivative of the "Simmons–Paquette molecule" **4**. The excessive steric bulk of the neopentane core of the triptyndantrione framework apparently favors the nucleophilic addition of the intermediate alcoholate to the *syn*-1,3-ethynyl group.<sup>[14]</sup> The intramolecular additions can be completed by treating the reaction mixture with aqueous sodi-

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Scheme 3. a)  $n\text{BuCCH}/n\text{BuLi}$ , THF,  $20^\circ\text{C}$ , then  $\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ ; b)  $\text{C}_2\text{H}_2$  or  $\text{PhCCH}/n\text{BuLi}$ , THF,  $T = -80^\circ\text{C} \rightarrow 20^\circ\text{C}$  or  $T = 20^\circ\text{C}$ , respectively, then  $\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ ; c) decalin,  $300^\circ\text{C}$ , 4 h; d) decalin,  $300^\circ\text{C}$ , 24 h; e)  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , diethylene glycol,  $\text{KOH}$ ,  $T = 140 \rightarrow 210^\circ\text{C}$ .

um carbonate; unfortunately, the yield of **11a** is only 25%. The analogous reaction with phenylacetylene provides **11b** in 27% yield, but so far the reaction with 1-hexyne has only given triol **10** ( $R = n\text{Bu}$ ).

Tris(enol ether)s **11** are characterized by mass spectrometry and IR and NMR spectroscopy (Table 1). The high molecular symmetry is reflected in the simple  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra; the AB pattern of the signals for the olefinic methylene protons of **11a** ( $^2J = 2.8$  Hz) is particularly characteristic. In the mass spectra of the enol ethers the elimination of up to three equivalents of CO is evident in the upper mass range. This indicates that heterocycles **11a** and **11b** rearrange to the corresponding carbocycles **13a** and **13b** not only in the mass spectrometer, but possibly also on the preparative scale. Whereas attempts with Brønsted and Lewis acids ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{THF}$ ,  $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$ ) and with  $\text{LiCl}_4/\text{ether}$ <sup>[15]</sup> were not successful, the thermolysis<sup>[16]</sup> of **11a** in decalin at  $300^\circ\text{C}$  provided the desired trione **13a** in 30%; **11b** was converted diastereoselectively into the triphenyl derivative **13b** in even 60% yield.<sup>[17]</sup> As expected, the mass spectra of the two triones are very similar to those of compounds **11**, but features typical of cyclopentanone rings are observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and IR spectra, for example an AB spectrum with  $^2J = -19.6$  Hz (**13a**). Thermolysis of **11a** for shorter periods resulted in the product of a single rearrangement, monoketone **12**. The parent compound of the new centrohexacycles, tribenzohexaquinane **14**, was obtained by Wolff-Kishner reduction of **13a** and also characterized unequivocally (Table 1).

We are currently trying to convert centrohexaquinanetrione **13** into the corresponding (unsaturated) tribenzocentrohexaquinanenes. These types of triquinanetriones and triquinanenes, which

Table 1. Physical and spectroscopic data for compounds **11**, **13**, and **14**.

**11a**: Colorless crystals, m.p.  $> 360^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 4.61, 4.67$  (AB spectrum,  $^2J = 2.8$  Hz, 6H), 7.38 (m, 6H), 7.54 (d, 3H), 7.78 (d, 3H); IR (KBr):  $\tilde{\nu} = 1656$   $\text{cm}^{-1}$  (C=C); MS (EI, 70 eV):  $m/z$ : 414 ( $M^+$ , 36), 386 (36), 358 (42), 330 (100); HRMS: ( $\text{C}_{29}\text{H}_{18}\text{O}_3$ ) calcd 414.1256; found 414.1265

**11b**: Colorless crystals, m.p.  $272^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 5.97$  (s, 3H), 7.14 (t, 3H), 7.30 (t, 6H), 7.41 (m, 6H), 7.66 (d, 6H), 7.74 (m, 3H), 7.80 (m, 3H); IR (KBr):  $\tilde{\nu} = 1671$   $\text{cm}^{-1}$  (C=C); MS (EI, 70 eV):  $m/z$ : 642 ( $M^+$ , 100), 614 (20), 586 (35), 558 (16); HRMS: ( $\text{C}_{29}\text{H}_{18}\text{O}_3$ ) calcd 642.2195; found 642.2186

**13a**: Colorless crystals, m.p.  $> 360^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 2.84, 3.27$  (AB spectrum,  $|^2J| = 19.6$  Hz, 6H), 7.30 (m, 9H), 7.84 (d, 3H); IR (KBr):  $\tilde{\nu} = 1745$   $\text{cm}^{-1}$  (C=O); MS (EI, 70 eV):  $m/z$ : 414 ( $M^+$ , 49), 386 (41), 358 (39), 330 (100); HRMS: ( $\text{C}_{29}\text{H}_{18}\text{O}_3$ ) calcd 414.1256; found 414.1257

**13b**: Colorless crystals, m.p.  $298^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 4.74$  (s, 3H), 6.34 (d,  $^3J = 7.8$  Hz, 3H), 6.50 (br. d,  $^3J = 7.0$  Hz, 6H), 6.90 (td,  $^3J = 7.5$  Hz,  $^4J = 0.8$  Hz, 3H), 7.05 (t,  $^3J \approx 7.5$  Hz, 6H), 7.14 (d,  $^3J \approx 7.4$  Hz, 3H), 7.27 (td,  $^3J = 7.5$  Hz,  $^4J = 0.9$  Hz, 3H), 7.82 (d,  $^3J = 7.8$  Hz, 3H); IR (KBr):  $\tilde{\nu} = 1741$   $\text{cm}^{-1}$  (C=O); MS (EI, 70 eV):  $m/z$ : 642 ( $M^+$ , 100), 614 (53), 586 (75), 558 (32); HRMS: ( $\text{C}_{47}\text{H}_{30}\text{O}_3$ ) calcd 642.2195; found 642.2194

**14**: Colorless crystals, m.p.  $264^\circ\text{C}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 1.93, 2.17$  (AA'BB' spectrum, 12H), 7.10–7.25 (m, 9H), 7.67 (d,  $^3J = 7.4$  Hz, 6H); MS (EI, 70 eV):  $m/z$ : 372 ( $M^+$ , 100), 358 (13), 343 (15), 329 (13), 316 (15);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 39.83$  (t,  $\text{CH}_2$ ), 65.88 [s,  $\text{C}(\text{C})(\text{Ar})(\text{CH}_2)_2$ ], 77.22 [s,  $\text{C}(\text{Ar})_3$ ], 123.58 (t), 124.25 (t), 127.58 (t), 127.63 (t), 148.36 (s), 150.34 (s), the signal of the centro-C atom is missing; HRMS: ( $\text{C}_{29}\text{H}_{24}$ ) calcd 372.1878; found 372.1879

have their convex molecular faces completely shielded,<sup>[18, 19]</sup> may be key intermediates in new, promising approaches to pentagon dodecahedranes from two triquinacene units.<sup>[18c, 18d, 20–22]</sup>

In conclusion we note that the propellane route described here for the construction of centrohexacyclic hydrocarbons may serve as an example of how the a priori unfavorable steric relations mentioned at the beginning of this report may also be advantageous for such compact structures. The remarkably facile formation of tris(enol ether) **11** is apparently a result of a proximity effect, and the subsequent consecutive rearrangements do not provide any possibility for the fragmentation of the molecular framework. The next particularly challenging step is determining whether the new propellane route leading to benzoannellated centrohexaquinanes like **9** and **14** may also be useful in the synthesis of the parent compound, centrohexaquinane **2**.

#### Experimental Procedure

**9**: A suspension of **6** (3.36 g, 10.0 mmol) in 250 mL of benzene was prepared with exclusion of air and moisture. A solution of phenyllithium (2M, 100 mL) in diethyl ether/cyclohexane was then added and the reaction mixture heated at  $40^\circ\text{C}$  for 12 h. After hydrolysis the organic phase was dried and concentrated, and the biphenyl formed removed by Kugelrohr distillation. The remaining triol **8** was dissolved in 250 mL of xylene and treated with 5 mL of orthophosphoric acid, and the reaction mixture was heated for 24 h with a water separator. After the reaction mixture had cooled, the organic layer was decanted off, dried over sodium sulfate, and concentrated. The brown residue was filtered over silica gel ( $\text{CHCl}_3$ ) and recrystallized from dichloromethane/hexane. Pure **9** (MS, NMR [5]) was obtained as colorless needles (2.07 g, 40%).

**11a** and **11b**: A suspension of **6** (3.36 g, 10.0 mmol) in 200 mL of THF was added dropwise over 30 min to a solution of lithium acetylide [23] (1.06 g, 33.0 mmol) in 200 mL of THF cooled at  $-90^\circ\text{C}$ . The temperature was not allowed to exceed  $-80^\circ\text{C}$  during the addition. After the addition was complete, the red-brown solution was stirred for 60 min before it was allowed to warm to room temperature. Water (80 mL) and then solid  $\text{Na}_2\text{CO}_3$  were added until the aqueous layer had a pulpy consistency. After a further 12 h of stirring, the organic layer was decanted off and the residue washed with  $\text{CHCl}_3$  ( $2 \times 200$  mL). The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$  and concentrated. Column chromatography on silica gel ( $\text{CHCl}_3/\text{hexane}$ ) provided **11a** (1.04 g, 25%). – When lithium phenylacetylide (3.57 g, 33.0 mmol) was used and the reaction conducted at room temperature, **11b** (1.73 g, 27%) was obtained after analogous workup.

**13a** and **13b**: A mixture of **11a** (200 mg, 480  $\mu\text{mol}$ ) or **11b** (200 mg, 310  $\mu\text{mol}$ ), 8 mg of hydroquinone, and 10 mL of anhydrous decalin was sealed under nitrogen in a thick-walled glass ampule and heated at  $300^\circ\text{C}$  in an oven for 24 h. After cooling to room temperature, the light brown reaction solution was treated with pentane to precipitate the product as a beige powder, which was washed with pentane and

purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate 60:1) to give **13a** (60 mg, 30%) or **13b** (120 mg, 60%).

**14:** Triketone **13** (16.0 mg, 38.6 μmol) was heated with 5 mL of diethylene glycol, 1 mL of hydrazine hydrate, and 50 mg of KOH at 140 °C for 3 h and then at 210 °C for 4 h. The reaction mixture was allowed to cool, 5 mL of water was added, and the mixture was extracted with CHCl<sub>3</sub> (2 × 10 mL). Filtration through silica gel (CHCl<sub>3</sub>) gave **14** (3.0 mg, 21%).

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## Base-Free Monomeric Organogallium Hydrides\*\*

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Information on neutral gallium mono- and dihydrides is quite sparse.<sup>[1]</sup> Structurally characterized examples of such species are confined to the dimers [Me<sub>2</sub>Ga(μ-H)]<sub>2</sub>,<sup>[2]</sup> [H<sub>2</sub>Ga(μ-Cl)]<sub>2</sub>,<sup>[3]</sup> [H<sub>2</sub>Ga(μ-NMe<sub>2</sub>)]<sub>2</sub>,<sup>[4]</sup> and [H<sub>2</sub>Ga(μ-H)<sub>2</sub>BH<sub>2</sub>]<sup>[5]</sup> and the novel monomer [HGa(BH<sub>4</sub>)<sub>2</sub>] with a pentacoordinate gallium atom.<sup>[6,7]</sup> However, the recent detection of the tricoordinate monomers GaHCl and GaH<sub>2</sub>Cl in argon matrices<sup>[8]</sup> suggested that monomeric organogallium hydrides might become isolable if sufficiently bulky substituents were employed.

Treatment of [Ga(Ar)Cl]<sub>2</sub><sup>[9]</sup> (Ar = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) with Li-GaH<sub>4</sub> in Et<sub>2</sub>O at –78 °C afforded a 73% yield of colorless crystalline **1**. In the CI mass spectrum of **1** the base peak appears at *m/z* 315 and corresponds to [Ga(Ar)H]<sup>+</sup>. This assignment was confirmed by a high-resolution mass spectrum (HRMS).<sup>[10]</sup> The detection of a terminal GaH<sub>2</sub> moiety in the neutral molecule was evident from the presence of infrared peaks in the terminal Ga–H stretching region (ν<sub>s</sub> = 1908 cm<sup>–1</sup>(sh), ν<sub>as</sub> = 1887 cm<sup>–1</sup>) and the relative intensities of the GaH<sub>2</sub> resonance and those of the aryl substituent in the <sup>1</sup>H NMR spectrum.<sup>[10]</sup> Moreover, the deshielded position of the GaH<sub>2</sub> resonance (δ = 6.41) was suggestive of a base-free product since, for example, amine-gallane adducts exhibit hydride resonances in the range δ = 4.5–5.0.<sup>[11]</sup> The monomeric nature of **1** was confirmed by an X-ray structure analysis.<sup>[12]</sup> Individual molecules of **1** (Fig. 1) reside on a crys-

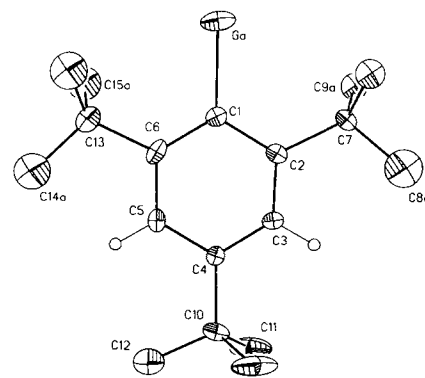
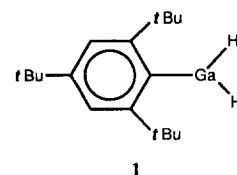


Fig. 1. View of **1** showing the atom labeling scheme. The *t*Bu groups at C2 and C6 are disordered and only the two highest occupancy methyl carbon atoms are shown. The hydrogen atoms on the gallium atom were not located. Selected distances [Å]: Ga–C1 1.942(7), Ga···C8 and Ga···C14 2.56(2).

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