Multiple Dissolving-Metal Reduction of Centropolyindans: Synthesis of a Hexakis(cyclohexano)centrohexaquinacene

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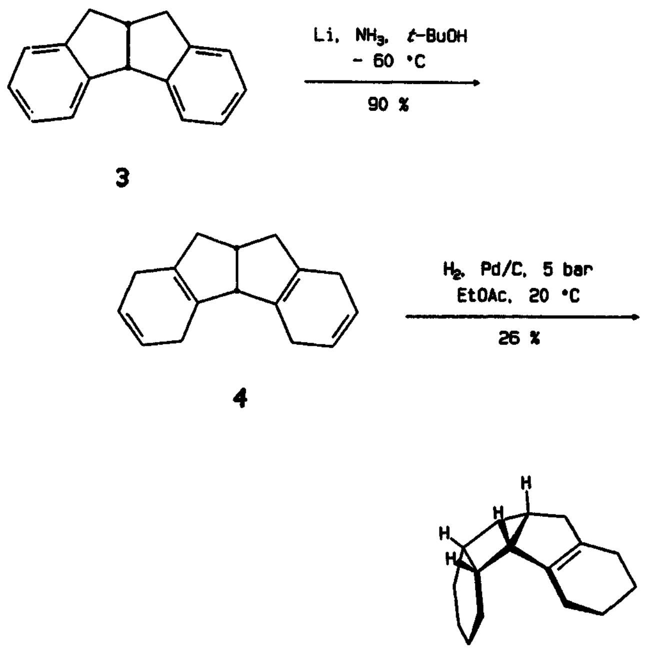
Abstract: Four prototype centropolyindans **1**, **3**, **7**, and **10** were subjected to reduction with Li/NH_3 and Li/NH_2Me. While Birch reduction of **1**, **3**, and **7** gives medium to good yields of the corresponding two-, three-, and sixfold 1,4-cyclohexadienes **2**, **4**, and **8**, respectively, centrohexaindan **10** does not react at all. With Li in NH_2Me, however, **10** is converted to the corresponding hexaene, the title compound **12**. Similarly, Benkeser reductions of **1** and **7** give the corresponding triquinacene **6** and the [3.3.3]propellatriene **9**. Preliminary epoxidation and hydrogenation experiments of some polycyclic olefins are presented.

The chemistry of polycondensed hydrocarbons incorporating cyclopentane subunits is of considerable interest. Five-membered rings enforce three-dimensionality into formally planar ring networks, and large variety of globular, spherical (bowl-shaped), and more complex truly "3D" structures including spiro centers have been synthesized in the field of polyquinanes.[1-8] Recently, additional strong impact comes from the advent of fullerene chemistry.[9]

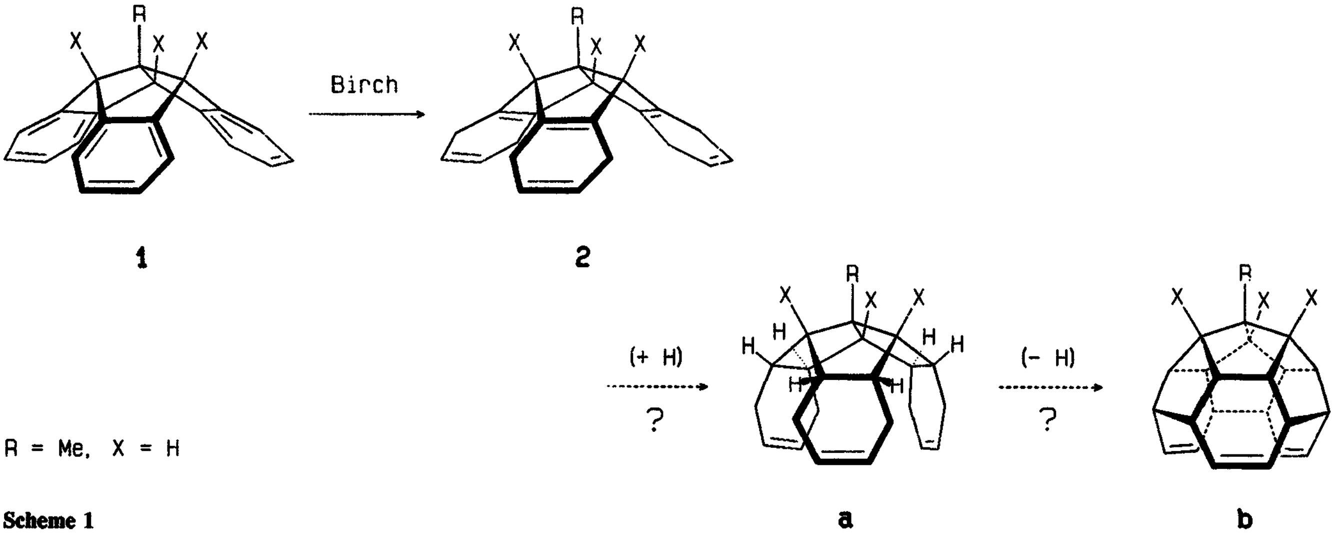
In centropolyindan hydrocarbons, studied by us for about a decade now,[10] a central "core" of two or several mutually fused cyclopentane rings bears several annelated benzo or areno groups, giving rise to 3D polycyclic structures. With the aim to utilize the peripheral benzene rings of the centropolyindans for the construction of more highly condensed spherical or even globular systems, as suggested in Scheme 1,[11] we started an investigation of partially hydrogenated and functionalized centropolyindans using Birch[12] and Benkeser[13] reduction techniques.[14] This paper gives a first report on the accessibility and limitations of centropolyindans containing 4,7-dihydro- and 4,5,6,7-tetrahydroindan [Δ(3a,7a),Δ(5,6) and Δ(4a,7a)hydrindan] units.

Treatment of the diindan **3** (Scheme 2) with lithium in liquid ammonia at − 60 °C gives the tetraene **4** in good yield.[15] Likewise, tribenzotriquinacene **1** and triptindan **7** are easily converted to the corresponding threefold Δ(3a,7a),Δ(5,6)-hydrindans **2** and **8**, respectively, with the former product being isolated in particularly good yields (Scheme 3). Similarly, use of lithium in methylamine as the solvent at − 30 °C leads to the corresponding threefold Δ(3a,7a)-hydrindans **6** and **9**, respectively.

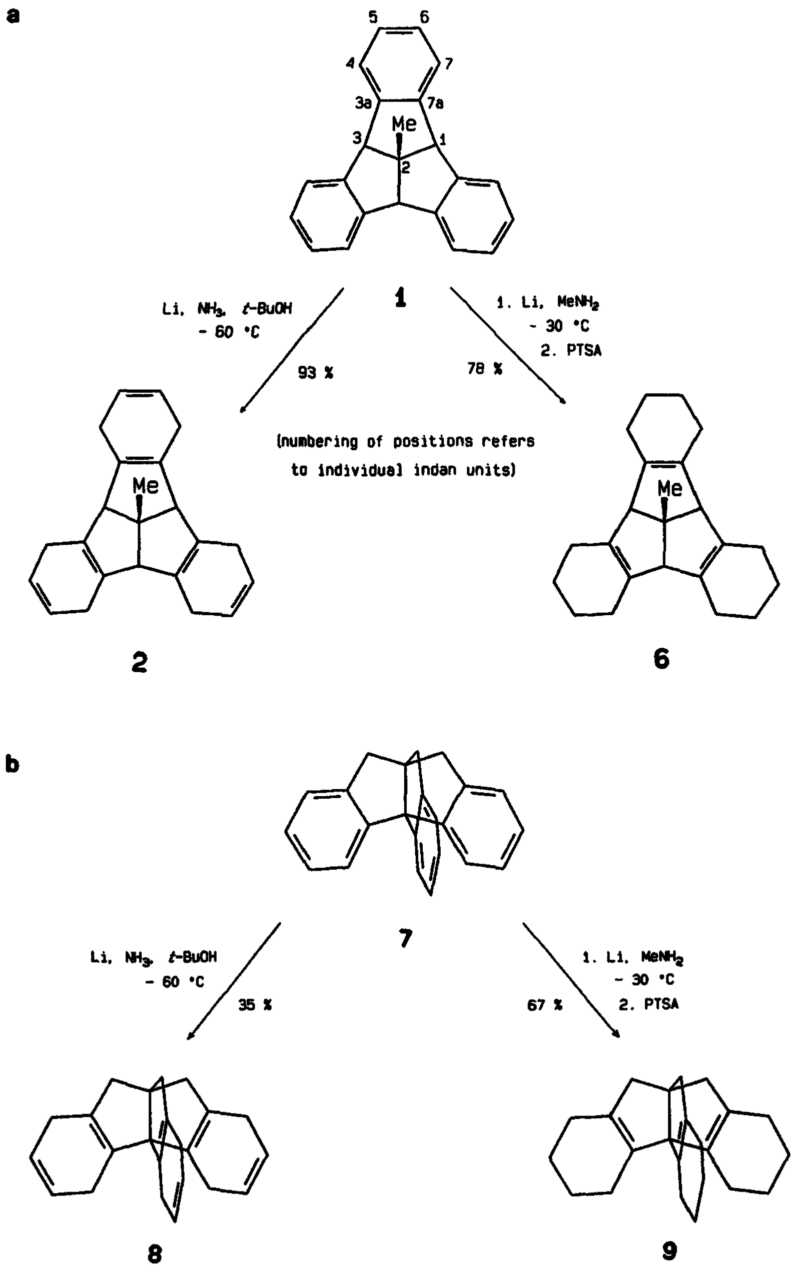


Scheme 2

The formation of overreduced polyindans is minimized by careful control of the excess lithium used. Moreover, Benkeser reduction gives varying amounts of trienes containing one or more Δ(3a,4) double bonds, which however are quantitatively isomerized to the more thermodynamically stable C_3-symmetrical products **6** and **9** by catalysis with *p*-toluenesulphonic acid.[16,17]



Scheme 1



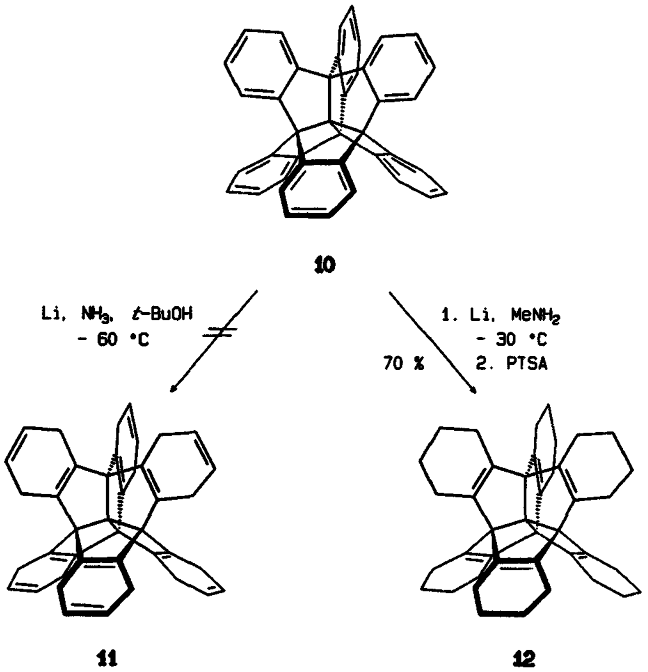
Scheme 3

Higher members of the centropolyindan family have also been subjected to Birch and to Benkeser reduction. However, severe limitations arise in some cases due to the low solubility of the educts. The most remarkable example here is centrohexaindan **10**, the highly condensed "regular" centropolyindan,[10] comprising six indan units (Scheme 4). All efforts to prepare the sixfold diene **11** under Birch conditions were unsuccessful, and **10** was recovered quantitatively in every case. Much to the contrary, Benkeser reduction of **10** does take place to give, after isomerization of the crude product, the sixfold Δ(3a,7a)]hydrindan **12**, hexakis(cyclohexano)-centrohexaquinacene,[18,19] in a remarkable 70 % yield.

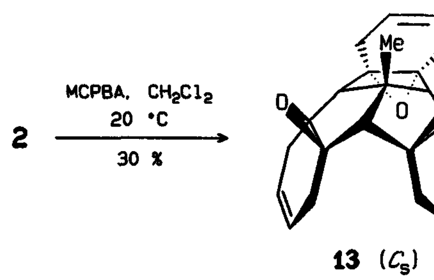
First attempts to stereoselectively hydrogenate the remaining double bonds of the polycyclic olefins showed severe sterical interactions of the six-membered rings. Thus, the tetraene **4** gives the monoolefin **5** obviously by exo attack at one of the Δ(3a,7a) double bonds (Scheme 2), but full hydrogenation was not achieved so far. Studies in this context comprise also epoxidation of the internal double bonds in order to "bend" the indan units. For example, reaction of **2** with *m*-chloroperbenzoic acid gives the C_s-symmetrical triepoxide **13**, which contains two mutually compressed cyclohexene rings (Scheme 5).[20] Further studies on the reduction and epoxidation of various higher centropolyindans are underway in our laboratories and will be reported in due course.

Birch Reduction of 1 (Typical Prodedure).

1,4,4b,5,8,8b,9,12,12b,12d-Decahydro-12d-methyldibenzo[2,3:4,5]-pentaleno[1,6-*ab*]pentalene. To a mixture of lithium (1.25 g, 180 mmol) in 500 ml of liquid ammonia held under nitrogen atmosphere at − 60 °C is added a solution of **1** (4.42 g, 15.0 mmol) and of *t*-butanol (13.0 g, 180 mmol) in 150 ml of dry tetrahydrofuran. The mixture is stirred at − 60 °C for 5 h, and then allowed to slowly warm up in the cooling bath. After evaporation of the ammonia the excess lithium is destroyed with methanol, and 200



Scheme 4



Scheme 5

ml of water is added. The mixture is extracted with diethyl ether, and the combined organic layers are washed with 1*N* hydrochloric acid and dried with sodium sulphate. Evaporation of the solvent gives a colourless residue which is recrystallized from dichloromethane/methanol to yield **2** as colourless needles (4.18 g, 93 %), mp 149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.70 (s, 6 H; 2,3,6,7,10,11-H), 2.76 (m_c, 15 H; 1,4,5,8, 9,12-CH_2, 4b,8b,12b-H), 1.33 (s, 3 H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 134.70 (q, C-4a,4c,8a,8c, 12a, 12c), 124.38 (t, C-2,3,6,7,10,11), 69.19 (t, C-4b,8b, 12b), 57.37 (q, C-12d), 28.19 (s, C-1,4,5,8,9,12), 27.27 (p, CH_3).

Benkeser Reduction of 1 (Typical Prodedure).

1,2,3,4,4b,5,6,7,8,8b,9,10,11,12,12b,12d-Hexadecahydro-12d-methyl-dibenzo[2,3:4,5]pentaleno[1,6-*ab*]pentalene. To a mixture of lithium (2.50 g, 360 mmol) in 600 ml of liquid methylamine held under nitrogen atmosphere is added at − 30 °C a solution of **1** (5.89 g, 20.0 mmol) in 150 ml of dry tetrahydrofuran. The mixture is stirred at − 30 to − 20 °C for 6 h and then allowed to slowly warm up in the cooling bath. After evaporation of the amine, the excess lithium is destroyed by addition of methanol. Work-up as described above gives a yellow oil, which is redissolved in 100 ml of dry dichloromethane. After addition of *p*-toluenesulphonic acid monohydrate (300 mg), the mixture is heated at reflux for 3 d. After evaporation of the solvent, the residue is subjected to chromatography (silica gel, *n*-hexane) to give pure **6** (4.80 g, 78 %) as colourless material, which may be recrystallized from dichloromethane/methanol to give colourless needles, mp 196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.61 (s, 3 H; 4b,8b,12b-H), 2.04 (m_c, 12 H; *allyl*-CH_2), 1.59 (m_c, 12 H, *homoallyl*-CH_2), 1.25 (s, 3 H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ = 137.28 (q, *olefin*-C), 69.93 (t, C-4b,8b, 12b), 57.41 (q, C-12d), 27.60 (p, CH_3), 26.36 (s, *allyl*-C), 22.91 (s, *homoallyl*-C).

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(17) No isomers with Δ(3,3a) double bonds (e.g. isotriquinacenes, cf. ref. 16) were observed, in line with the mechanism of the reduction reactions.

(18) Compound **12** may be referred to as hexakis(cyclohexano)-C_{17}-hexaquinacene; see Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600.

(19) **Hexakis(cyclohexano)centrohexaquinacene(12);1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,19,20,21,22,25,26,27,28-Tetracosahydro-4b,12b[1',2']:8b,16b[1",2"]dibenzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene:** mp > 360 °C; IR (KBr) $\nu = 2927\ cm^{-1}$, 2881, 2855, 2836, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 2.22$ (br s, 24 H; *allyl*-CH_2), 1.60 (br s, 24 H, *homoallyl*-CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta = 139.36$ (q, *olefin*-C), 83.41 (q, C-16d), 78.66 (q, C-4b,8b,12b, 16b), 26.96 (s, *allyl*-CH_2), 23.04 (s, *homoallyl*-CH_2); MS (70 eV) m/z (%) 540 (100, $M^{\cdot +}$), 460 (5), 458 (4), 270 (15, M^{2+}). Calcd for $C_{41}H_{48}$: C 90.64, H 8.95; Found C 91.05, H 8.90.

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