Irregular Centropolyindans: Synthesis of 4b,9,13b,18-Tetrahydroindeno[1,2-*a*]indeno[2'',1''-*b*']indeno[1',2'-*b*]indene and Other Novel Centrotriindans[1]

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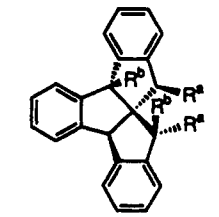
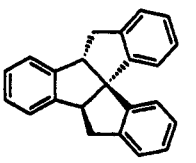
The syntheses of a novel tetraindan **6**, containing two contiguous quaternary central carbon atoms, and of a number of other derivatives of the (unknown) "irregular" centrotriindan **5**, is reported. Two-fold bridgehead benzylation of the C_2-symmetrical diindandione **7** followed by reduction leads to the dibenzyldiindandiols **11**, which undergo 2-fold acid-catalyzed cyclodehydration (H_3PO_4/chlorobenzene) in moderate yield (22%) to **6**. In contrast, use of xylene as the solvent gives rise to a Wagner–Meerwein rearrangement along with a single cyclodehydration step producing benzylidenetriindan **14** in good yield (70%). Monobenzyldiindandiols **10** incorporate a solvent molecule upon cyclodehydration in *p*-xylene to give triindan **12**, whereas use of chlorobenzene yields complex mixtures of triindene **13** and its oligomers. These results shed some light on the relatively high strain of the tetraquinane skeleton of **6** and, in particular, on the reactivity of bridgehead [Δ(9b,10)]-diindenes, in line with previous results. An independent attempt to generate **6** from 2,2'-biindanyltetrol **16** gave the dibenzodioxatetraquinane **17** in low yield.

In 1981, Gund and Gund[2] published a classification scheme of complex polycyclic organic ring systems bearing a carbon atom which is shared by all of the rings. Among these *centropolycyclanes*,[2] centropoly*quinanes*, i.e., those congeners bearing mutually fused cyclopentane units, have been of particular interest because of their relation to naturally occurring[3,4] and non-natural model[5-7] systems and because of the favorable steric fit of centrically fused five-membered rings.

Centropolyindans, the benzoannelated analogues of centropolyquinanes, obey the same classification scheme.[8] During the past decade, all higher members of the family of "regular" centropolyindans have been synthesized in our laboratory,[9-11] including various centrotriindans and centrotetraindans (e.g., **1**,[10a,11d] and, respectively, **2**[10b,11d] and **3**[11b]) and the highest possible congeners, centropentaindan[12] and centrohexaindan.[13]





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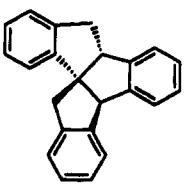
1, $R^a = R^b = H$

2, $R^a - R^a = o\text{-}C_6H_4$; $R^b = H$

3, $R^a = H$; $R^b - R^b = o\text{-}C_6H_4$



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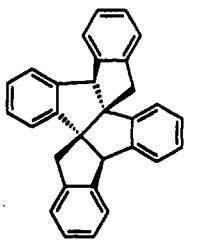

6

"Irregular" Centropolyindans

All these centropolyindans may be termed "regular" because of the formal annelation of (up to six) benzo nuclei at the C_2 units bridging the central neopentane core. Thus, formally, the regular triindan **1** may be extended in this manner to the next-higher regular centrotetraindans **2** and **3** and, eventually, to centropenta- and centrohexaindan.

In contrast, "irregular" centropolyindans do not fit this simple scheme. In these congeners, at least one of the benzo nuclei includes an α carbon atom of the C(C_4) core. Centrotriindan **4**, which was described by Ten Hoeve and Wynberg,[14] may serve as an example. In this triindan, representing an isomer of **1** and having been the highest irregular centropolyindan known prior to our work, two benzo nuclei are directly linked to the C(C_4) core.[15]

® Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Benzoannelated Centropolyindans. 16. Parts 15 and 14: ref 11c and d, respectively.

(2) Gund, P.; Gund, T. M. *J. Am. Chem. Soc.* **1981**, *103*, 4458.

(3) (a) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry, Synthesis and Reactions*; Springer: Berlin, 1987. (b) Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41. (c) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1.

(4) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141.

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(9) Paisdor, B.; Kuck, D. *J. Org. Chem.* **1991**, *56*, 4753.

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(11) Recent papers: (a) Kuck, D.; Lindenthal, T.; Schuster, A. *Chem. Ber.* **1992**, *125*, 1449. (b) Kuck, D.; Seifert, M. *Chem. Ber.* **1992**, *125*, 1461. (c) Kuck, D.; Neumann, E.; Schuster, A. *Chem. Ber.* **1994**, *127*, 151. (d) Kuck, D. *Chem. Ber.* **1994**, *127*, 409.

(12) Kuck, D.; Schuster, A.; Gestmann, D. *J. Chem. Soc., Chem. Commun.* **1994**, 609.

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(14) Ten Hoeve, W.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2930.

(15) Other pairs of regular and irregular centro"poly"indans, respectively, are 2,2'-spirobiindan vs 1,1'-spirobiindan and the (C_s- vs C_2-symmetrical) fusodiindans (for spiro- and fusodi*quinanes*, cf. ref 2).

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Noteworthily, this type of benzoannelation does not allow one to add more than four benzo units to one neopentane core, instead of six in the regular centropolyindans.[16]

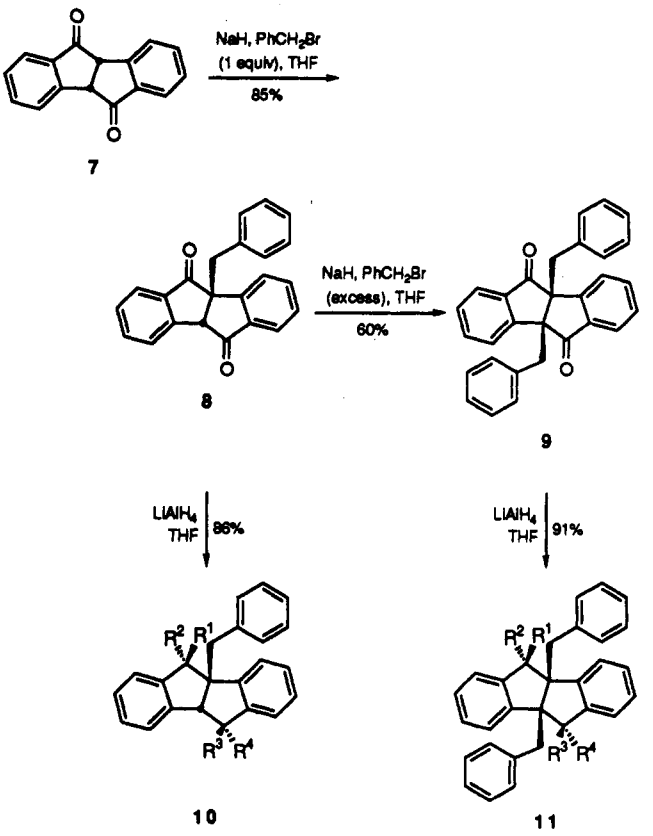
In this paper, we present the syntheses of several derivatives of the irregular centrotriindan **5**, the "missing" isomer between **1** and **4**. Among these, the novel tetraindan **6** is particularly interesting[17] since it contains two contiguous quaternary carbon centers at the bridgehead positions of mutually fused C_s-diindan subunits, similar to the tetraindan **3** and its higher regular congeners. It was anticipated that the formation of *two* adjacent quaternary carbon centers[18,19] would markedly increase the strain of the polyquinane framework of **6**. Since the syntheses of many of the regular centropolyindans were achieved by acid-catalyzed cyclodehydration of suitable 1-indanols and 1,3-indandiols,[11] we wished to examine the accessibility of **6** using similar synthetic strategies.

Results and Discussion

The synthesis of **6** was started from C_2-diindanone **7**, which has been described by several authors.[20] Best results for bridgehead benzylation of **7** were obtained by sequential treatment of this ketone with 1 equiv of NaH and benzyl bromide in THF at reflux temperature to give the monobenzyl diketone **8** in 85% isolated yield. This material was then reacted under the same conditions but with a 100% excess of the reagents to furnish the (4bα,9bα)-dibenzyldiindanone **9** in 60% isolated yield. One-pot 2-fold benzylation of **7** under various conditions was found to be unfavorable, giving only minor yields of **9** together with several *O*-benzylation products.

Reduction of the diindandiones **8** and **9** with excess $LiAlH_4$ in THF gave, in both cases, mixtures of three diastereomeric diindandiols in >90% yield. Column chromatography of the monobenzyl diols **10** yielded the pure "*exo,exo*" (5α,10α)-diastereomer **10a** as a minor component (ca. 2%) and a mixture (84%, ca. 1:1) of the two major isomers, viz. "*exo,endo*"-, i.e., (5α,10β)-diol **10b** and "*endo,endo*"-(5β,10β)-diol **10c**, which could not be separated. The mixture of dibenzyldiindandiols **11** consisted of one major diastereomer, viz. "*exo,exo*"-(5α,10α)-diol **11a**, which was obtained pure by recrystallization (78% yield).

Scheme 1[a]



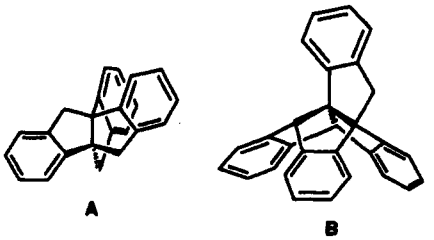
	R^1	R^2	R^3	R^4	yield (%)
10a	OH	H	OH	H	2[a]
10b	OH	H	H	OH	>40[b]
10c	H	OH	H	OH	>40[b]
11a	OH	H	OH	H	78[a]

[a] Key: (a) isolated; (b) isolated as a 1:1 mixture.

Stereochemical identification of **10a–10c** and **11a** was achieved by ^1H NMR spectrometry showing characteristic vicinal coupling and AB spin patterns. Thus, the spectra of the major diols **10b** and **10c** displayed large vicinal H–H coupling constants, $^3J_{9b-10}$, and largely different or, respectively, very close chemical shifts for the methylene protons (**10b**, $\Delta\delta_{CH_2} = 0.59$, and **10c**, $\Delta\delta_{CH_2} = 0.06$), whereas the "*exo,exo*" diol **10a** showed a low $^3J_{9b-10}$ value and, akin **10b**, an "extended" *AB* spin pattern ($\Delta\delta_{CH_2}$ = 0.52 ppm). These features, together with the 2-fold degeneracy of all ^1H resonances, allowed unequivocal stereochemical identification of the major dibenzyldiindandiol as the C_2 symmetrical "*exo,exo*" isomer **11a** ($\Delta\delta_{CH_2}$ = 0.65).

With both diketones **8** and **9**, the stereochemistry of the diols obtained clearly reflects the stereocontrol of the attack of the $LiAlH_4$ reagent by the benzyl group(s) above the convex diindan "surface", in line with previous results.[11] In general, the AlH_4^- ion attacks preferentially at the "exo" side of a diindanone C=O group, if that side is not heavily shielded by other substituents. With suitable *diones*, another hydride ion may be transferred *within* the complex from the $ROAlH_3^-$ grouping to the second C=O group, in competition with a bimolecular exo attack of a second

(16) Besides **4** and **5**, tribenzo[3.3.3]propellane **A** would represent another irregular centrotriindan, and tetraindan **B**, as an isomer of **2** and **3**, would be the highest possible irregular centropolyindan. Both **A** and **B** or their derivatives are hitherto unknown. For the regular congener of **A**, see ref 9 and references cited therein.



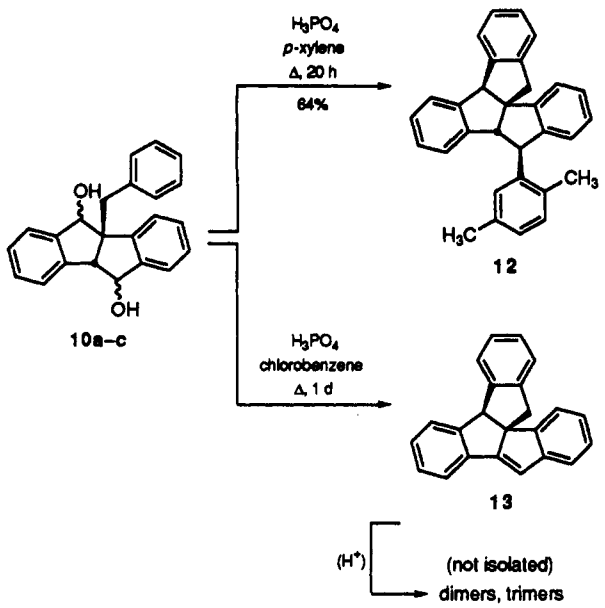
(17) The tetraquinane corresponding to **6** has been described: (a) Venkatachalam, M.; Jawdosiuk, M.; Desphande, M. N.; Cook, J. M. *Tetrahedron Lett.* **1985**, *26*, 2275. (b) Venkatachalam, M.; Kubiak, G.; Cook, J. M.; Weiss, U. *Tetrahedron Lett.* **1985**, *26*, 4863. (c) Venkatachalam, M.; Desphande, M. N.; Jawdosiuk, M.; Kubiak, G.; Wehrli, S.; Cook, J. M.; Weiss, U. *Tetrahedron* **1986**, *42*, 1597.

(18) Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

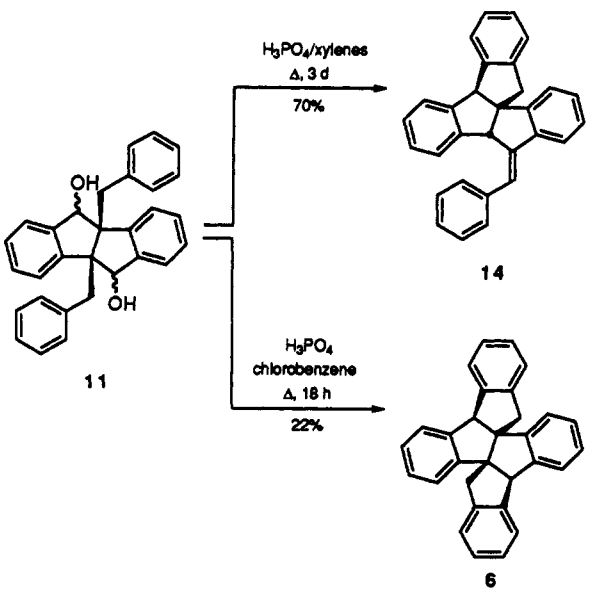
(19) For polyspiranes containing several contiguous quaternary carbon atoms, see: (a) Fitjer, L.; Justus, K.; Puder, P.; Dittmer, M.; Hassler, C.; Noltemeyer, M. *Angew. Chem.* **1991**, *103*, 431; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 436. (b) Fitjer, L.; Quabeck, U. *Angew. Chem.* **1989**, *101*, 55; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 94.

(20) (a) Wawzonek, S. *J. Am. Chem. Soc.* **1940**, *62*, 745. (b) Mittal, R. S. D.; Sethi, S. C.; Dew, S. *Tetrahedron* **1973**, *29*, 1321. (c) Ogura, F.; Nakao, A.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1980**, *45*, 2930.

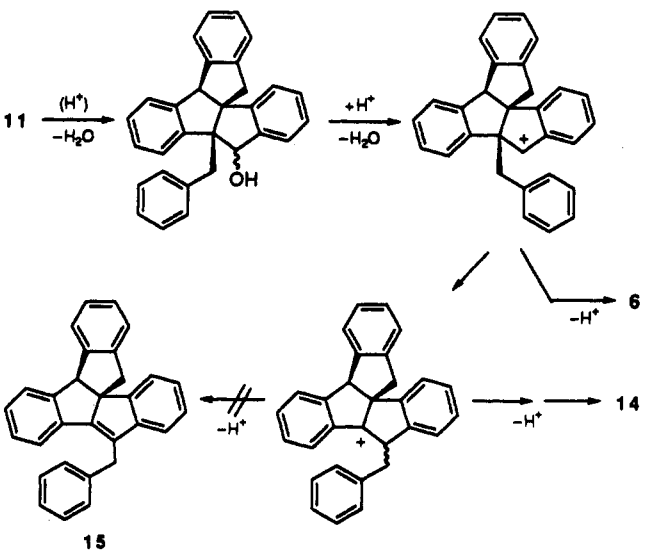
Scheme 2



Scheme 3



Scheme 4



AlH_4^- ion at that C=O group.[11a,21] Accordingly, dione **8** reacts preferentially by primary "exo" attack at the easily accessible C(10)=O group to give the major isomers **10b** and **10c**, respectively. In contrast, the two vicinal, mutually repelling benzyl groups in dione **9** efficiently shield the α sides of both C=O groups, thus forcing two (intermolecular) "endo" attacks of the reagent to give diol **11a** as the major stereoisomer.

Attempts to perform a combined cyclodehydration/1,2-elimination of water of diols **10** were unsuccessful (Scheme 2). Under standard conditions (H_3PO_4/*p*-xylene at 140 °C), one solvent molecule was incorporated giving the 10α-xylyl-substituted triindan **12**.[22] With chlorobenzene as a less electron-rich solvent, arylation was suppressed; instead, mixtures were obtained which, according to NMR and MS analysis, contained only minor amounts of triindene **13** (not isolated pure), along with several products derived from intermolecular C–C coupling of two or three diindans. Obviously, the bridgehead double bond in **13** is very reactive under the relative harsh conditions of cyclodehydration.[23]

In contrast to diols **10**, dibenzyldiindanols **11** exhibited a more clearcut cyclodehydration behavior (Scheme 3). With H_3PO_4 in xylene, surprisingly, benzylidenetriindan **14** was formed in 70% isolated yield. Again, a single cyclodehydration occurred but was accompanied, in this case, by a Wagner–Meerwein rearrangement of the second benzyl group and sequential hydride shifts, thus omitting the formation of the unfavorable Δ[C(9b)–C(10)] bridgehead olefin **15** (Scheme 4). This parallels the behavior of the monobenzyldiindandiols **10** discussed above. ^{1}H NMR spectrometry of **14** points to the *trans*-stilbene-type stereoisomer.

Heating **11** with H_3PO_4 in chlorobenzene at reflux temperature for 18 h furnished a yellow oil from which the title centrotetraindan **6** was isolated pure by column chromatography in 22% yield. In more polar fractions, considerable amounts of aldehydes were obtained as byproducts (see Experimental Section). Upon prolonged heating, the yield of **6** did not increase; instead, mixtures of **6** and benzylidenetriindan **14** were obtained containing increasing relative amounts of the rearrangement product. Noteworthily, extended heating of "pure" mixtures of **6** and **14** did not affect their ratio; thus, the formation of both hydrocarbons is irreversible under the conditions used. The formation of aldehydes points to Grob fragmentation, again in line with previous results,[11a,b] of the diindan moiety in ionic intermediates generated by the 1,2-benzyl shift, possibly *preceding* the first cyclodehydration step. Further work is required to clarify the course of these multistep reactions.

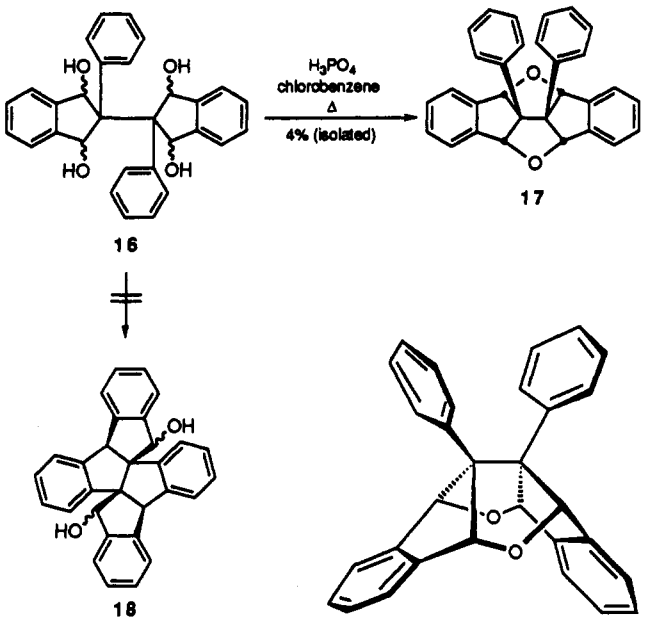
The C_2 molecular symmetry of **6** is reflected by the simple NMR spectra. The ^{13}C NMR spectrum displays three lines for the tetraquinane core and four lines for the benzo junctions. Accordingly, the ^{1}H NMR spectrum shows only one AB spin pattern for the two methylene groups, one singlet for the two benzhydryl bridgehead protons, and three distinct multiplets for the four sets of 2-fold degenerate *ortho*-protons. The 70-eV electron impact (EI) mass spectrum of **6** indicates the molecular

(21) (a) Cawley, J. J.; Petrocine, D. V. *J. Org. Chem.* **1976**, *41*, 2608. (b) Cawley, J. J.; Petrocine, D. V. *J. Org. Chem.* **1975**, *40*, 1184.

(22) (a) The *anti* orientation of the xylyl group follows from the low vicinal coupling constant ($^3J_{9b,10}$ < 2 Hz). (b) Two other xylyl isomers of **10** were obtained using *m*-xylene or a commercial mixture of the xylenes (mp 239 °C, 37% yield, and mp 158 °C, 63%, respectively); Eckrich, R. Ph.D. Thesis, University of Bielefeld, 1993.

(23) If possible, "exocyclic" bridgehead double bonds in diindenes tend to be shifted into the diquinane C–C junction under cyclodehydration conditions (cf. ref 11c).

Scheme 5



ion (m/z 382) as the base peak and only minor fragmentation, in great contrast to the partially cyclized triindan 14 ($[M^{\bullet+} - C_7H_7]:[M^{\bullet+}] = 0.92$).

As an alternative approach to tetraindan 6, we tried to perform a 2-fold cyclodehydration of the 2,2′-biindanyltetrol 16[24] with H_3PO_4 in chlorobenzene. Not surprisingly, however, a multicomponent mixture of products was formed, in which the presence of the expected product of double cyclodehydration, dihydroxytetraindan 18, was suggested by the EI mass spectrum showing an apparent molecular ion peak (m/z 414). Therefore, the mixture was subjected to hydrogenolysis (Pd/C, EtOAc) but, instead of 6, dibenzodioxatetraquinane 17, as an isomer of 18, was isolated as the only product in low yield (4%).[25]

In conclusion, the experiments reported here show that the irregular centrotetraindan 6 is synthetically accessible by the 2-fold cyclodehydration already used for the synthesis of a number of other centropolyindans (e.g., 1 and 2) from 1,3-indandiols.[10,11a,d] However, some limits of this cyclization method have emerged, notwithstanding the fact that two single, formally independent cyclodehydration steps are required to generate the polyindan framework of 6. In contrast to some higher, *regular* centropolyindans such as 2 and its synthetical precursors, two mutually bonded quaternary carbon atoms are created, which leads to an increased steric strain in this irregular centropolyindan.[26] Owing to the lack of intramolecular stabilization by embedding these two quaternary centers in a completely closed, e.g., propellane-type substructure (such as in 3), the system tends to escape, at least in part, from the 2-fold cyclodehydration route by rearrangement to 14.

Experimental Section

General Methods. Melting points are uncorrected: Büchi 521 or Electrothermal melting point apparatus. IR spectra: Perkin-Elmer 841; KBr platelets. ^{1}H NMR spectra: Bruker AM 300; solvent $CDCl_3$ with $Si(CH_3)_4$ used as internal standard. ^{13}C NMR spectra: Bruker AM 300; solvent $CDCl_3/Si(CH_3)_4$, broadband decoupling, J-modulated spin-echo experiments. Mass spectra: Finnigan MAT CH5, Fisons (VG Analytical) Auto-spec; electron impact (EI, 70 eV). Combustion analyses: Perkin-Elmer 240. Column chromatography: Kieselgel 60, 0.063–0.200 mm (Merck, Macherey & Nagel). Thin-layer chromatography: Kieselgel 60 F_{254} on Al foil (Merck).

(4bα,9bα)-4b-Benzyl-4b,5,9b,19-tetrahydroindeno[2,1-*a*]indene-5,10-dione (8). A suspension of 1.80 g (60.0 mmol) of sodium hydride (80% in paraffin) in 150 mL of dry THF was stirred and heated to reflux as a solution of 11.7 g (50.0 mmol) of diindandione 7 in 200 mL of the same solvent was added within 20 min. After the mixture was heated for another 15 min, a solution of 10.3 g (60.0 mmol) of benzyl bromide in 50 mL of dry THF was added, and the mixture was stirred and heated to reflux for 15 h. After the mixture was cooled to rt, excess sodium hydride was destroyed with ice/water, and the greenish precipitate was removed by filtration. Evaporation of the solvent left a dark oil which was crystallized from chloroform/methanol to give 13.7 g (85%) of 8 as colorless crystals: mp 157 °C; IR (KBr) 3065, 2926, 1708, 1596, 1459, 1284, 764, 719, 705 (cm^{-1}); ^{1}H NMR (300 MHz) δ 8.03 (m_c; 1 H), 7.73 (m_c; 3 H), 7.59 (m_c; 2 H), 7.41 (m_c; 2 H), 7.12 (m_c; 3 H), 7.00 (m_c; 2 H), 4.20 (s; 1 H; 9b-H), AB (δ_A 3.62, δ_B 3.28, $^2J_{AB}$ = −13.7 Hz; 2 H; CH_2); ^{13}C NMR (75 MHz) δ 207.76 [quat. C; C(5)=O], 201.25 [quat. C; C(10)=O], 153.45, 148.95, 136.33 (all quat. C), 135.69 (tert. C), 134.45 (quat. C), 129.59, 129.27, 128.94, 128.32, 126.90, 126.18, 125.54, 124.66, 124.47 (all tert. C), 61.72 (quat. C; C-4b), 56.74 (tert. C; C-9b), 41.21 (sec. C; CH_2); MS m/z 324 (46, $M^{\bullet+}$), 333 (100), 205 (11), 176 (11), 151 (5), 91 (15). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.17; H, 5.09.

(4bα,9bα)-4b,9b-Dibenzyl-4b,5,9b,10-tetrahydroindeno-[2,1-*a*]indene-5,10-dione (9). A suspension of 3.00 g (100 mmol) of sodium hydride (80% in paraffin) in 250 mL of dry THF was stirred and heated to reflux as a solution of 16.2 g (50.0 mmol) of 8 in 250 mL of the same solvent was added within 25 min. After 15 min, a solution of 17.1 g (100 mmol) of benzyl bromide in 50 mL of dry THF was added, and the mixture was stirred and heated to reflux for 21 h. Cooling and hydrolyzation gave a mixture from which the inorganic salts were removed by filtration through silica. Evaporation of the solvent gave a yellow oil which was crystallized from ethanol and yielded 12.4 g (60%) of 9 as colorless crystals: mp 129 °C; IR (KBr) 3032, 2932, 1708, 1596, 1460, 1284, 768, 721, 694 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.69 (m_c; 2 H), 7.53 (m_c; 4 H), 7.41 (m_c; 2 H), 7.08 (m_c; 6 H), 6.71 (m_c; 4 H), AB (δ_A 3.77, δ_B 3.41, $^2J_{AB}$ = −15.6 Hz; 4 H; CH_2); ^{13}C NMR (75 MHz) δ 203.66 [quat. C; C(5)=O, C(10)=O], 153.45, 136.85 (both quat. C), 134.99 (tert. C), 133.32 (quat. C), 129.91, 129.29, 127.91, 126.36, 126.05, 124.71, (all tert. C), 65.07 (quat. C; C-4b, C-9b), 38.31 (sec. C; CH_2); MS m/z 414 (38, $M^{\bullet+}$), 323 (100), 305 (21), 295 (17), 279 (10), 265 (19), 189 (10), 105 (17), 91 (44), 65 (8). Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.62; H, 5.67.

(4bα,9bα)-4b-Benzyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene-5,10-diol (10, Isomers 10a–10c). A suspension of 760 mg (20.0 mmol) of lithium aluminum hydride in 100 mL of dry THF was stirred as a solution of 3.24 g (10.0 mmol) of 9 in 50 mL of the same solvent was added, and the mixture was heated to reflux for 17 h. After the mixture was cooled and hydrolyzed with ice/water, the hydroxides were removed by filtration, and the filtrate was diluted with dichloromethane (100 mL) and dried with Na_2SO_4. Removal of the solvent gave 3.12 g (95%) of diol 10 as a mixture of isomers, which may be used for cyclodehydration (see below) without further purification: IR (KBr) 3378, 3065, 3030, 2915, 1602, 1493, 1477, 1453, 1206, 1103, 1047, 761, 702 cm^{-1}; MS m/z 328 (0.6, $M^{\bullet+}$), 310 (39), 323 (100), 305 (21), 105 (17), 91 (45). Column chromatography through silica with dichloromethane/ethyl acetate (9:1) furnished a pure isomer (10a) as a minor component and a mixture of nonseparated isomers (10b and 10c, ca. 1:1) as the major components.

(4bα,5α,9bα,10α)-4b-Benzyl-4b,5,9b,10-tetrahydroindeno-[2,1-*a*]indene-5,10-diol (10a): yield 68 mg (2%), slightly yellow solid; ^{1}H NMR (300 MHz) δ 7.69 (d; ^3J = 7.7 Hz; 1 H), 7.29 (m_c; 10 H), 6.83 (m_c; 2 H), 5.36 (s; 1H; 5-H), 4.89 (s; 1 H; 10-H), 3.64 (s; 1 H; 9b-H), AB (δ_A 3.62, δ_B 3.10, $^2J_{AB}$ = −13.3 Hz; 2 H; CH_2).

(24) Behringer, F. M.; Galton, S. A.; Huang, S. J. *Tetrahedron* **1963**, *19*, 809.

(25) The parent dioxatetraquinane has been described: Mehta, G.; Reddy, K. R. *J. Org. Chem.* **1987**, *52*, 460.

(26) (a) Force field calculations (ref 26b) suggest that formal annellation of two lateral indan units to the C_2-diindan basis in 6 causes an increase of strain by a factor of ca. 2.5 as compared to annellation of only one, as in 5. (b) Allinger, N. L., MM 2 (87), QCPE, University of Indiana, 1987.

(4bα,5α,9bα,10β)-4b-Benzyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene-5,10-diol (10b) and (4bα,5β,9bα,10β)-4b-benzyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene-5,10-diol (10c) (mixture of isomers): yield 2.77 g (84%), slightly yellow solid; ^{1}H NMR (300 MHz) δ 7.60 (d; ^3J = 7.6 Hz; 1 H), 6.82 (m_c; 2 H), 6.76 (m_c; 2 H), 5.30 (s; 1 H; 5-H), 4.97 (s; 1 H; 5-H), 4.83 (d; ^3J = 7.3 Hz; 1 H; 10-H), 4.43 (d; ^3J = 7.9 Hz; 1 H; 10-H), 4.09 (d; ^3J = 7.9 Hz; 1 H; 9b-H), 3.79 (d; ^3J = 7.3 Hz; 1 H; 9b-H), AB (δ_A 3.46, δ_B 2.87, $^2J_{AB}$ = −13.6 Hz; 2 H; CH_2), AB (δ_A 3.28, δ_B 3.22, $^2J_{AB}$ = −13.2 Hz; 2 H; CH_2), 1.85 (br s; OH); ^{13}C NMR (75 MHz) δ 146.23, 145.43, 145.20, 145.09, 144.32, 142.13, 140.66, 139.03, 138.32, 137.63 (all quat. C), 130.02, 129.00, 128.91, 128.82, 128.32, 128.24, 128.18, 127.97, 127.88, 127.74, 127.51, 126.51, 126.30, 126.17, 125.70, 125.38, 124.33, 124.01 (all tert. C), 82.32, 81.57, 75.53, 74.67 (all tert.; C-5, C-10), 64.29, 63.47 (both quat. C; C-4b), 56.74, 56.44 (both tert. C; C-9b), 42.53, 40.31 (both sec. C; CH_2).

(4bα,5α,9bα,10α)-4b,9b-Dibenzyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene-5,10-diol (11a). A suspension of 2.66 g (70.0 mmol) of lithium aluminum hydride in 150 mL of dry THF was stirred as a solution of 14.5 g (35.0 mmol) of **10** in 170 mL of the same solvent was added, and the mixture was heated to reflux for 1 d. Workup as described above furnished 13.3 g (91%) of **11a** as a colorless solid containing isomeric diols to a minor extent. Recrystallization from ethyl acetate/ethanol yielded 11.5 g (78%) of pure **11a** as fine, colorless crystals: mp 250 °C; IR (KBr) 3535, 3399, 3067, 3030, 2935, 1601, 1476, 1453, 1432, 1381, 1201, 1117, 1083, 1069, 763, 742, 703 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.20 (m_c; 10 H), 7.05 (m_c; 4 H), 6.92 (m_c; 4 H), 5.23 (d; ^3J = 8.5 Hz; 2 H; 5-H, 10-H), AB (δ_A 3.69, δ_B 3.05, $^2J_{AB}$ = −13.3 Hz; 4 H; CH_2), 1.70 (d; ^3J = 8.5 Hz; 2 H; OH); MS *m/z* 400 (3, [M − H_2O]$^{\bullet+}$), 309 (21), 291 (9), 231 (18), 203 (14), 189 (12), 178 (16), 165 (8), 91 (100), 65 (6). Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.46; H, 6.08.

9β-(2′,5′-Dimethylphenyl)-4bα,8bβ,9,14-tetrahydrodiindeno[1,2-a:1′,2′-b]indene (12). According to the procedure given above, benzyldiindandiol **10** (3.25 g, 9.9 mmol) was reacted in 100 mL of *p*-xylene as the solvent. Workup as described above yielded an oily residue which was crystallized from ethyl acetate/ethanol to give 2.56 g (64%) of **12b** as a slightly yellow powder: mp 150 °C; IR (KBr) 3068, 3022, 2921, 1499, 1478, 1454, 820, 756 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.28 (m_c; 12 H), 7.07 (d; ^3J = 7.5 Hz; 1 H, 3′-H), 6.95 (d; ^3J = 7.5 Hz; 1 H, 4′-H), 6.48 (s; 1 H, 6′-H), 4.84 (s; 1 H; 4b-H), 4.75 (s; 1 H; 9-H), 3.61 (s; 1 H; 8b-H), AB (δ_A 3.45, δ_B 3.20, $^2J_{AB}$ = −16.6 Hz; 2 H; CH_2), 2.53 (s; 3 H; 1′-CH_3), 2.21 (s; 3 H; 5′-CH_3); ^{13}C NMR (75 MHz) δ 149.39, 146.15, 145.32, 144.47, 143.78, 141.90, 135.47, 132.48 (all quat. C), 131.00, 130.35, 127.73, 127.61, 127.55, 127.33, 127.05, 127.00, 126.98, 125.95, 124.68, 124.45, 124.23, 123.36 (all tert. C), 67.44 (quat. C; C-13b), 64.91 (tert. C; C-4b), 63.37 (tert. C; C-9), 54.22 (tert. C; C-8b), 46.60 (sec. C; C-14), 21.19 (prim. C; CH_3), 20.11 (prim. C; CH_3); MS *m/z* 398 (92, M$^{\bullet+}$), 292 (100), 215 (14), 178 (23), 146 (14), 91 (10). Anal. Calcd for $C_{31}H_{26}$: C, 93.42; H, 6.58. Found: C, 93.65; H, 6.30.

Dehydration of 8 with H_3PO_4/Chlorobenzene. Attempts to Synthesize Triindene 13. A solution of 6.23 g (19.0 mmol) of benzyldiindandiol **10** (mixture of isomers) in 150 mL of chlorobenzene and 2 mL of orthophosphoric acid (85%) were stirred and heated to reflux for 1 d with separation of the reaction water. The hot solution was decanted from the catalyst by pouring it through K_2CO_3, and the solvent was removed in vacuo. The oily residue was subjected to column chromatography [silica, n-hexane/dichloromethane (2:1)]. The first eluting fraction (ca. 152 mg) was a mixture containing ca. 55% of **4b,14-dihydroindeno[1,2-a:1′,2′-b]indene (13)** along with a pertinacious impurity, which could not be separated. The identity of **13** was indicated the molecular ions peak [EI-MS: *m/z* 292 (100, M$^{\bullet+}$)] and by a characteristic resonances in the ^{1}H NMR spectrum (300 MHz), in particular at δ 6.71 (s; 1 H; olefinic 9-H). The following two fractions (712 and 161 mg) were mixtures which, according to MS analysis, contained mainly dimers of **13** [e.g., *m/z* 584 (100, M$^{\bullet+}$), 493 (17), 381 (16), 292 (93), 207 (40), 178 (28), 91 (28)]. The fourth fraction (542 mg) contained dimers and trimers of **13** [e.g., MS *m/z* 876 (34, M$^{\bullet+}$), 584 (32), 292 (61), 207 (100), 177 (52), 91 (28).

(*E*)-9-Benzylidene-4bα,8bβ,14-trihydrodiindeno[1,2-a:1′,2′-b]indene (14). A solution of 7.53 g (18.0 mmol) of dibenzyldiindandiol **11a** in 350 mL of dry xylene (mixture of isomers) and 5 mL of orthophosphoric acid (85%) were stirred and heated to reflux for 3 d with separation of the reaction water. The catalyst and the solvent were removed as described above to give a colorless oil; crystallization from chloroform/*n*-hexane yielded 4.86 g (70%) of **14** as fine, colorless needles: mp 212 °C; IR (KBr) 3064, 3027, 2926, 1478, 1459, 768, 750, 737, 695 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.60 (m_c; 2 H), 7.33 (m_c; 5 H), 7.21 (m_c; 5 H), 7.13 (m_c; 6 H), 5.09 (s; 1 H), 4.61 (s; 1 H), AB (δ_A 3.72, δ_B 3.44, $^2J_{AB}$ = −17.1 Hz; 2 H; CH_2); ^{13}C NMR (75 MHz) δ 147.76, 145.57, 144.93, 144.68, 143.24, 142.48, 141.15, 136.28 (all quat. C), 129.26, 128.76, 128.07, 127.51, 127.33, 127.15, 126.61, 125.23, 124.69, 124.39, 124.26, 123.76, 121.96, 120.52 (all tert. C), 65.34 (tert. C), 64.39 (quat. C; C-13b), 58.49 (tert. C), 45.62 (sec. C; C-14); MS *m/z* 382 (100, M$^{\bullet+}$), 303 (24), 291 (92), 289 (40), 202 (8), 178 (10), 152 (11), 151 (10), 91 (8). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.40; H, 5.80.

4bα,9,13bα,18-Tetrahydroindeno[1,2-a]indeno[2″,1″-b′]indeno[1′,2′-b]indene (6). A solution of 837 mg (2.00 mmol) of dibenzyldiindandiol **11a** in 25 mL of chlorobenzene and 0.5 mL of orthophosphoric acid (85%) were stirred and heated to reflux for 18 h with separation of the reaction water. The catalyst and the solvent were removed as described above to give a yellow oil which was subjected to column chromatography (*n*-hexane/chloroform). As the first-eluted fraction, 172 mg (22%) of **6** were obtained as fine, colorless needles: mp 200 °C (from $CHCl_3$/*n*-hexane); IR (KBr) 3068, 3022, 2926, 2878, 1479, 1456, 768, 750, 695 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.48 (m_c; 2 H), 7.38 (m_c; 2 H), 7.31 (m_c; 2 H), 7.21 (m_c; 10 H), 4.83 (s; 2 H; 4b-H, 13b-H), AB (δ_A 3.19, δ_B 3.06, $^2J_{AB}$ = −17.2 Hz; 4 H; 9- and 18-CH_2); ^{13}C NMR (75 MHz) δ 149.06, 144.62, 144.16, 142.29 (all quat. C), 127.56, 127.22, 126.95, 124.35, 124.26, 124.09, 123.88 (all tert. C), 69.11 (quat. C; C-8b, C-17b), 63.82 (tert. C; C-4b, C-13b), 43.54 (sec. C; C-9, C-18); MS *m/z* 382 (100, M$^{\bullet+}$), 366 (12), 305 (19), 303 (16), 291 (16), 289 (19), 203 (13), 178 (13), 151 (14), 91 (7). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.51; H, 5.67.

The second fraction (140 mg of a yellow oil) represented a mixture containing two aldehydes, which have not completely been identified.[22b] Major component: ^{1}H NMR (300 MHz) δ 10.10 (s, 1 H), 7.87 (m, 1 H), 6.9–7.4 (m), 6.71 (d, 1 H), 5.58 (s, 1 H), 4.12 (br s, 2 H), 4.01 and 3.27 (AB spin system, ^2J = −15.1 Hz, 2 H)]; MS *m/z* 400 (18, M$^{\bullet+}$), 382 (100, [M − H_2O]$^{\bullet+}$), 309 (45), 291 (80), 91 (94).

Cyclohydration of 9a in Chlorobenzene (Variant A). A mixture of 837 mg (2.00 mmol) of **11a**, 0.5 mL of orthophosphoric acid (85%), and 25 mL of chlorobenzene was reacted for 1 d and then worked up as described above. Column chromatography (*n*-hexane/chloroform) gave two fractions, the first of which represented a mixture of 259 mg (34% yield) of **6** (75%) and **14** (25%, by ^{1}H NMR). The second fraction is a yellow oil containing two aldehydes (see above). In a similar run, heating for 2 d gave an oily yellow residue which was crystallized from chloroform/*n*-hexane to give 370 mg (24% yield) of the mixture of **6** (38%, by ^{1}H NMR) and **14** (62%). Repeated heating of such isolated mixtures of **6** and **14** under standard reaction conditions (H_3PO_4/chlorobenzene) for 2 d had no effect on the ratio **6**:**14**.

10c,10d-Diphenyl-4bα,5aα,9bα,10aα,10cα,10dα-hexahydro-5,10-dioxadiindeno[1,3-c,d:1′,3′-g,h]pentalene (17). A solution of 785 mg (2.00 mmol) of **16**[24] in 30 mL of chlorobenzene and 0.4 mL of orthophosphoric acid (85%) were stirred and heated to reflux for 70 h with separation of the reaction water. Usual workup gives a red-brown solid, which was redissolved in 50 mL of ethyl acetate and, after addition of 110 mg of palladium-on-charcoal (Merck), subjected to hydrogenolysis at 4.6 bar/rt for 44 h. Removal of the catalyst gave a deeply colored filtrate from which, upon standing for several days, a poorly soluble solid precipitated as colorless, brilliant needles representing dibenzodioxatetraquinane **17** (35 mg, 4.2%): mp > 380 °C; IR (KBr) 3033, 2956, 1446, 1231, 1069, 954, 904, 763, 743, 697 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.39 (d; ^3J ≈ 8.3 Hz, 4 H), AA′BB′ (δ_A 7.14, δ_B 7.00; 8 H), 7.05 (t; ^3J = 7.5 Hz, 4 H), 6.93 (t; ^3J = 7.3 Hz, 2 H), 4.83 (s; 4 H; 4a-,5a-,9a-,10a-H); MS *m/z* 414 (19, M$^{\bullet+}$, 296 (36), 292 (61), 281 (100), 207 (53), 191 (41), 178 (45), 165 (27), 105 (75), 77 (16). Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 87.14; H, 5.05.

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