Benzoanellated Centropolyquinanes, 11[1]

Synthesis of Tribenzotriquinacene and Some *centro*-Substituted Derivatives☆

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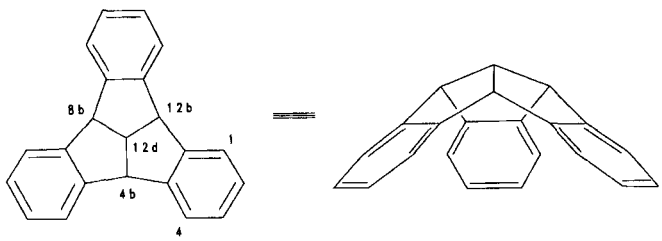
The syntheses of tribenzotriquinacene (**1a**) and five *centro*-substituted derivatives, **1b**–**1e** and **1g**, as well as of the related diindan **13** are reported. The three-step synthetic sequences include the reduction of suitably substituted 2-benzhydryl-1,3-indandiones **3** to the corresponding 1,3-indandiols **4** and the twofold cyclodehydration of the latter to close two additional five-membered rings at a time. Although the yields of the cyclodehydration step **4** → **1** are only low to moderate (10–33%), the overall approach allows the preparation of 5–50-gram amounts of the centropolyindans in most cases by starting from simple 1,3-indandiones **2a**–**2c**. This includes the new synthesis of the parent tribenzotriquinacene (**1a**). The related C_s-symmetrical diindan, 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene (**13**), has been prepared in high yield by using the same cyclodehydration technique. Scope and limitations of the double cyclodehydration strategy are described concerning the synthesis of 1,3-indandiones with bulky substituents at C-2 and the cyclization of 1,3-indandiols with an aptitude to undergo heterolytic cleavage of an exocyclic C-2–C-α bond, in particular **4f**. The course of the reduction of the 2,2-disubstituted 1,3-indandiones with lithium aluminum hydride is discussed on the basis of the stereochemistry of the product 1,3-indandiols.

Tribenzotriquinacene (**1**) (*trifuso*-centrotriindan[2]) is an interesting araliphatic hydrocarbon with a particularly rigid, C_{3v}-symmetrical, cup-like molecular framework consisting of three mutually fused indan units. By extending the three "trefoil leaves" of the triquinacene core with benzo groups the molecule of **1** gains not only considerable stabilization, as compared to triquinacene itself, but also enhanced reactivity at the three equivalent bridgehead positions. Since our



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first publication on the synthesis of tribenzotriquinacenes **1b**, **1d**, and **1e** by a double-cyclization strategy[3], the chemistry of these polycycles and related centropolyindans[2] has been extended[1,4–7]. In the meantime, the parent compound **1a** has been synthesized by a stepwise sequence[4,5a]. In the present paper, we report in detail on the synthesis of both **1a** and its 12d-(*centro*-)alkyl-substituted derivatives **1b**–**1e** and **1g** by the double cyclodehydration of the corresponding 1,3-indandiols **4**.

The Double-Cyclodehydration Strategy

The general synthetic approach to the tribenzotriquinacenes **1** is outlined in Scheme 1. It starts from 1,3-indandione (**2a**) or singly 2-alkyl-substituted derivatives **2b**–**2f**, which are converted into the corresponding 2-alkyl-2-benzhydryl-1,3-indandiones **3**. As will be shown, the diones **3a**–**3g** are accessible in this way. The sequence of the introduction of the substituents at C-2 may be varied; but some limitations to the overall dialkylation have become evident, as will be discussed below.

Prior to double cyclization the diones **3** are reduced to the corresponding 2-benzhydryl-1,3-indandiols **4**. In contrast to the chemistry of 1,3-indandiones, that of 1,3-indandiols has hardly been developed. While no problems have been encountered upon reduction of the (non-enolizable) 2,2-disubstitued 1,3-diones **3b**–**3g**, the clean twofold reduction of monosubstituted analogues such as **3a** is difficult. This has been one reason for the development of our stepwise synthesis of **1a**[4,5a]. A point of independent interest has been the stereochemical course of the reduction of 1,3-indandiones[8] with complex hydride reagents, which will be considered for the series **3b**–**3g** in the present work as well.

The key step in the synthesis of **1**, as well as of many other centropolyindans[2,9], is the double cyclodehydration of the 1,3-indandiols **4**. By utilizing appropriate substrates and reaction conditions, the double-cyclodehydration strategy provides a remarkably direct and efficient synthetic access to tribenzotriquinacenes. However, some limits of this approach will be discussed below.

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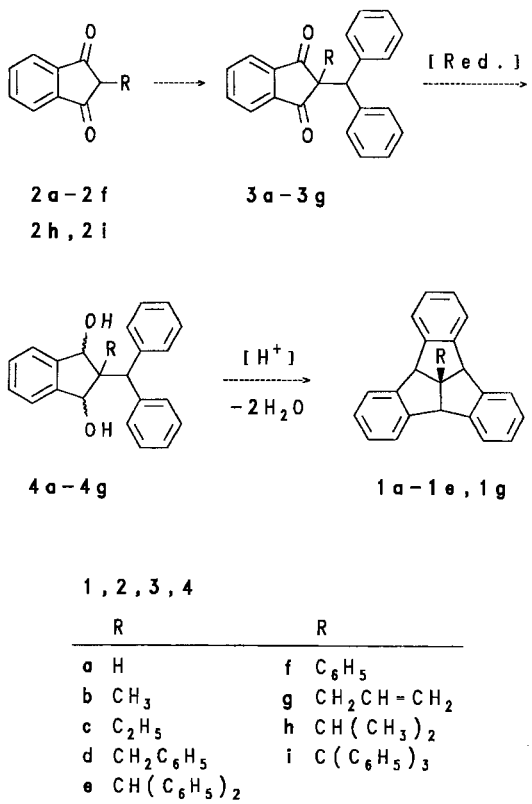
Scheme 1

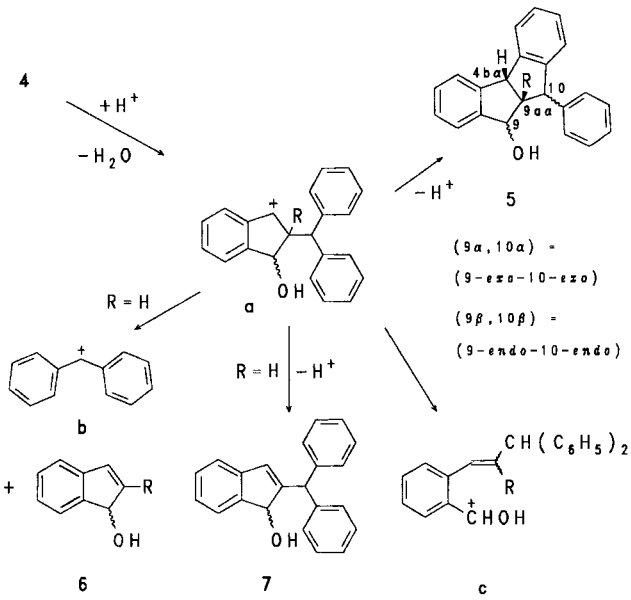


While the single cyclodehydration of carbonyl compounds bearing γ- or δ-aryl groups is part of the wealth of the electrophilic aromatic substitution chemistry and has been applied extensively[2,10,11], the dehydrating cyclization of γ- or δ-aralkyl alcohols has not gained much relevance[10]. The twofold cyclodehydration of diols had not been reported at all prior to our first paper[3,12]. Schönberg et al. reexamined the acid-catalyzed dehydration of two 1,3-indandiols[13a] and 2,2-spirobiindan-1,1′-diols[13b] and found that the overall reaction is governed by a cleavage of the 1,3-diol system, i.e., by an acid-catalyzed Grob fragmentation. Touron and Laude[14] found that 2,2-diaryl-1,3-indandiols rearrange upon treatment with acid to 2,3-diaryl-1-indanones.

As far as the double-cyclodehydration step **4** → **1** is concerned, our approach appeared challenging because of at least three unfavorable factors (Scheme 2). Two of them refer to the cleavage of fragile C–C bonds in the β-position to the incipient carbenium ion centre (**a** → **b** and **a** → **c**), and, in fact, evidence has been found for both fragmentation processes. The third unfavorable factor originates from the prochirality of the benzhydryl group. Two stereoisomers (**5**) were to be expected as intermediate products of the first ring closure, but only one of them, the disfavored *endo* isomer, should be prone to undergo the second cyclodehydration.

Curiously enough, the Grob-type fragmentation represents the major path under certain dehydration conditions [e.g., with *p*-toluenesulfonic acid (PTSA) as the catalyst][3]; this finding may be used to prepare interesting *mono*-dehydration products, as will be reported separately[15].

As a mechanistically related fragmentation path, the elimination of the electrofugic benzhydryl group (**a** → **b**) has been found to occur as well. While this side reaction does not interfere severely in most cases it indicates, however, one of the limits of our approach: benzhydryl-type groups of higher electrofugacity like the trityl substituent[16] (see below) do not undergo the double cyclodehydration but react exclusively by elimination.



The synthesis of unsubstitued tribenzotriquinacene (**1a**) represented a particular problem. Here, of course, 1,2-elimination of water dominates the reaction of the monosubstituted diol **4a**, leading to indenol **7** (Scheme 2) as an intermediate which should not readily undergo the desired twofold cyclization[10c,17]. In this case, a stepwise synthesis has been developed first[4,5a]; however, as will be shown in the present paper, modified reaction conditions allow to perform the direct, double cyclodehydration of **4a** to **1a** as well.

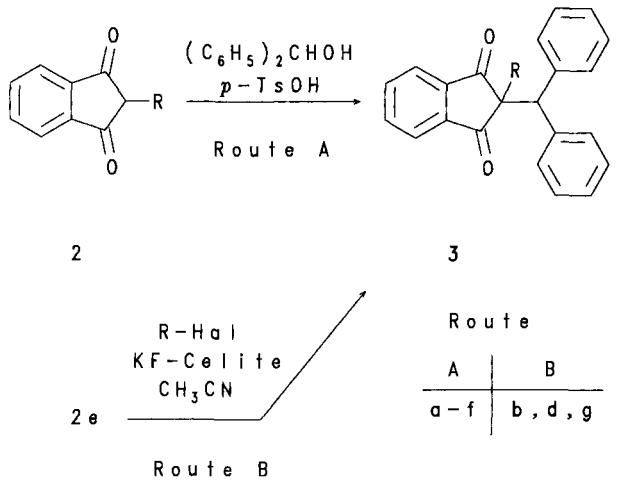
The three stages of the syntheses of the tribenzotriquinacenes **1a**–**1e** and **1g** are described in the following sections as well as some cases in which the cyclodehydration approach fails.

The Synthesis of 2-Benzhydryl-1,3-indandiones

2-Benzhydryl-1,3-indandione (**3a** ≡ **2e**) can be prepared by either a stepwise procedure or by acid-catalyzed alkylation of **2a** with benzhydrol, as described by de Winter and Nauta[18]. In our hands, the latter method proved to be more useful and has also been applied to the synthesis of 2-benzhydryl-1,3-indandiones **3b**–**3f** bearing another substituent at C-2 (Scheme 3). The yields of these alkylation reactions are in the range of 85–92%. Remarkably, we also obtained 2,2-dibenzhydryl-1,3-indandione (**3e**) by a simple one-step dialkylation of **2a**. While de Winter and Nauta isolated **3e** as a byproduct in the synthesis of **3a** from **2a**, this sterically crowded dione can be easily obtained in >75% yield as a pure, colorless powder. By contrast, 2-isopropyl-1,3-indandione (**2h**), which is readily synthesized in analogy to the

standard procedure used for **2b**, does not react with benzhydrol. This reflects the sensitivity of the (reversible) C–C bond formation to the steric conditions in the 2-position of 1,3-indandiones.

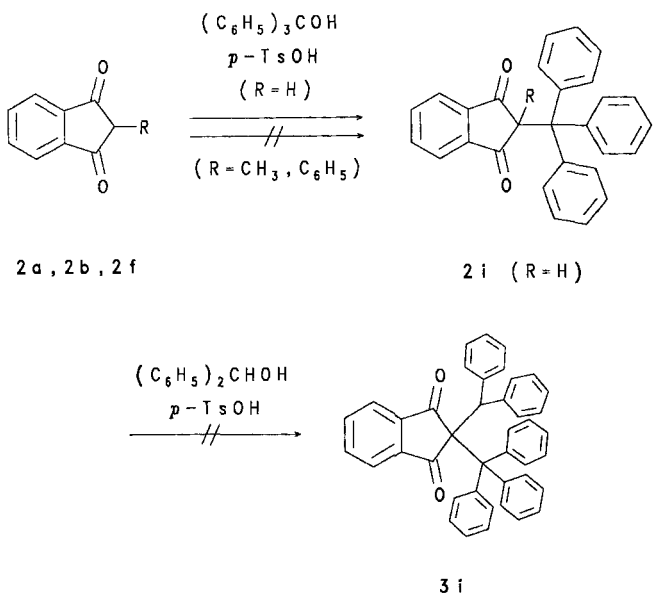
Scheme 3



We also performed the tritylation of **2a** with tritanol to give 2-trityl-1,3-indandione (**2i**) in 62% yield, but the subsequent introduction of a benzhydryl group to form **3i** failed (Scheme 4). A synthesis of **2i** has been described previously[19]. Likewise, the monosubstituted diones **2b** and **2f** did not react with tritanol[20]. Attempts to prepare 2-alkyl-2-trityl-1,3-indandiones by base-assisted methylation, allylation, or benzylation of **2i** led quantitatively to the corresponding enol ethers[17].

On the other hand, 2-alkyl-2-benzhydryl-1,3-indandiones can be prepared in this way. Thus, **3b**, **3d**, and **3g** have been

Scheme 4

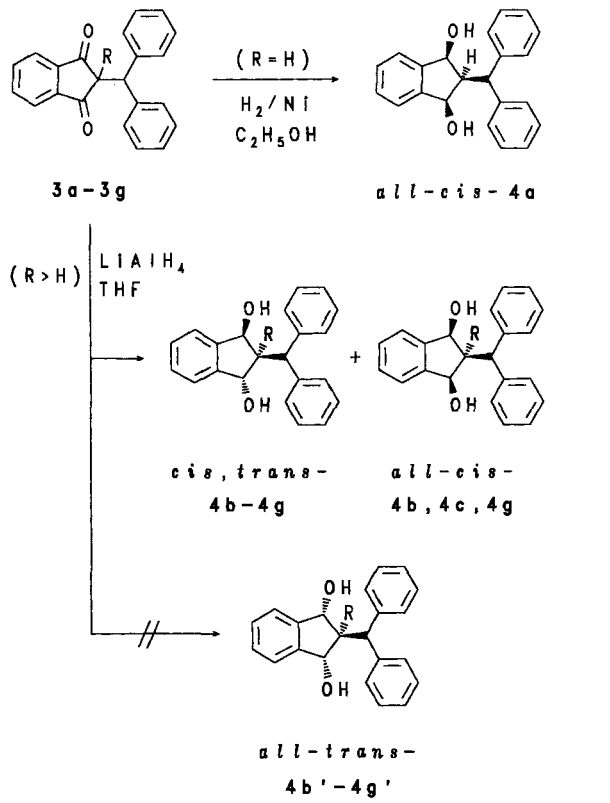


synthesized by using either NaH in DME or KF/Celite in acetonitrile[3]. The latter method, adopted from Bloch and Orvane[21], has been used preferably in these and related alkylation reactions. *C*-alkylation predominates, but 5–20% of the corresponding *O*-alkylation products is also observed. The results on *C*- cersus *O*-alkylation of 1,3-indandiones with KF/Celite will be published separately.

2-Benzhydryl-1,3-indandiols

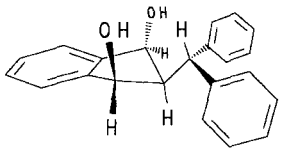
Due to their high C–H acidity, the reduction of monosubstituted 1,3-indandiones to 1,3-indandiols with complex hydrides does not occur in satisfactory yields. This holds also for the 2-benzhydryl-1,3-indandione (**3a**). We found, however, that benzhydryl-1,3-indandiol **4a** can be prepared in 70% yield by carefully controlled catalytic hydrogenation of dione **3a** with highly active Raney nickel at room temperature (Scheme 5). Reduction to 2-benzhydrylindan is frequently observed with the highly active catalyst at prolonged reaction times, whereas deactivated Raney nickel gives mainly the corresponding 1,3-ketol.

Scheme 5



Only one stereoisomeric diol, *all-cis*-**4a**, is obtained under these conditions. The C_s molecular symmetry of this isomer is reflected by the degenerate resonances in the ^{13}C-NMR spectrum as well as by the ^{1}H-NMR spectrum, which shows a characteristic doublet of triplets for 2-H. The remarkably large spin coupling between this proton and the benzhydrylic one ($^3J_{2,\alpha}$ = 12.2 Hz) as well as a small coupling with the two equivalent carbinol protons ($^3J_{1,2} = {}^3J_{2,3}$ = 4.5 Hz)

suggest that this diol is efficiently locked in the *anti* conformation shown in Figure 1[22].



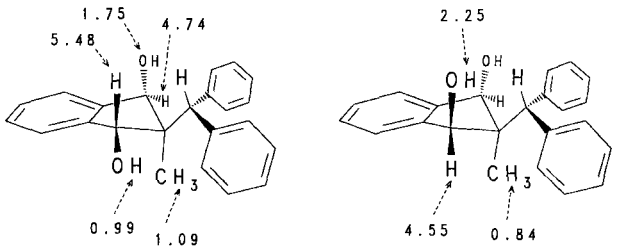
all-cis-4a

Figure 1. Preferred conformation of *all-cis*-2-benzhydryl-1,3-indandiol (*all-cis*-**4a**)

In contrast to **3a**, the 2,2-disubstituted 1,3-indandiones are readily reduced with lithium aluminium hydride in tetrahydrofuran (Scheme 5). Reduction of **3b** gives a mixture of two isomeric 1,3-indandiols in quantitative yield, the *trans*-1,3-diol (*cis,trans*-**4b**, 75%) and a *cis*-diol (*all-cis*-**4b**, 25%), as revealed by ^{1}H-NMR spectroscopy. Both isomers may be obtained as crystalline materials by fractional crystallization.

cis-trans-**4b** is clearly identified and distinguished from the two possible *cis* diastereomers by the observation of two AX spin systems for the two stereochemically distinct carbinol groupings. Characteristic deshielding effects of the benzhydryl group on the *cis*- and *trans*-OH groups and decoupling experiments with the resonances of the carbinol groups allow the complete assignment of the individual ^{1}H-NMR signals (Scheme 6)[23]. In contrast, *all-cis*-**4b** is characterized by degenerate carbionol AX spin systems. It can be readily distinguished from the hypothetical isomer (*all-trans*-**4b'**) by the pronounced deshielding of the two hydroxy protons. Correspondingly, the methyl proton signal of *all-cis*-**4b** exhibits a high-field shift due to the lack of deshielding *cis*-OH groups, in contrast to *cis,trans*-**4b** which bears one OH group *cis* to the methyl substituent. Additional support for the stereochemical assignment of *cis,trans*-**4b** and *all-cis*-**4b** is provided by the mechanistic arguments concerning the $LiAlH_4$ reduction (see below).

Scheme 6



cis,trans-4b *all-cis*-4b

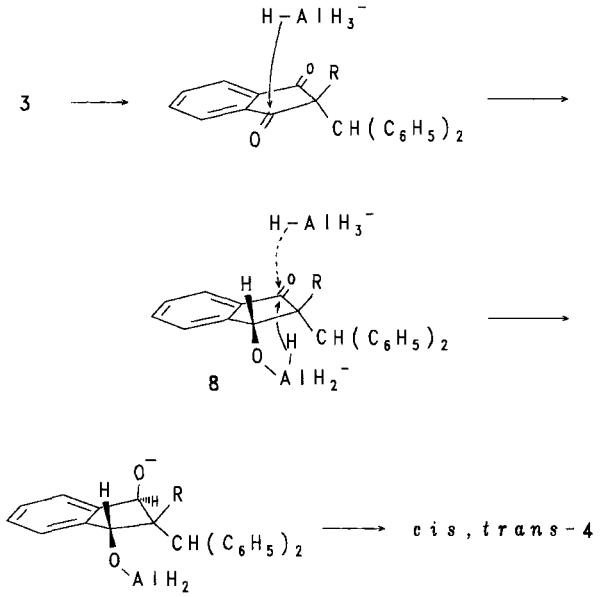
The ^{13}C-NMR spectra of *cis,trans*-**4b** and *all-cis*-**4b** also reflect the different molecular symmetries (C_1 and C_s, respectively). Whereas the spectrum of the *cis*-diol clearly exhibits eight degenerate lines, that of the *trans* isomer displays two different carbinol signals and signals of diastereotopic phenyl groups within the benzhydryl moiety. The latter features have also been observed for all other *trans*-1,3-indandiols described here.

Similar to **3b**, reduction of dione **3c** gives 2-benzhydryl-2-ethyl-1,3-indandiol (**4c**) in nearly quantitative yield. The ^{1}H-NMR analysis of the crude product reveals that again the *cis,trans* isomer (70%) and the *all-cis* isomer (30%) are formed. Similarly, the 2-allyl derivative **3g** gives *cis,trans*- and *all-cis*-**4g** in a ratio of 69:31. In all these cases, the diasteromers have been separated by fractional crystallization.

Reduction of all other 2,2-disubstituted 1,3-indandiones (**3d**–**3f**) with $LiAlH_4$/THF provides exclusively the corresponding *trans*-indandiols (*cis-trans*-**4d**, -**4e**, and -**4f**). In this context, the clean reduction of the sterically crowded bis(benzhydryl)dione **3e** to the corresponding *trans*-diol **4e** is remarkable. Therefore, it appears that only the extremely different bulkiness of the substituents at C-2 of the diones (methyl, ethyl, or allyl versus benzhydryl) allows the formation of the *all-cis*-1,3-indandiols as minor reduction products. (A partial reduction of **3e** to ketol **4e''** has been performed as well; see Experimental.)

The reduction of non-enolizable 1,3-diketones with complex hydrides has been investigated previously[8,24], and an "intramolecular" mechanism of the second reduction step has been discussed in several cases. Cawley and Petrocine[8] studied this problem with 2,2-dimethyl-1,3-indandione and related compounds. These authors disfavored the intramolecular mechanism as the governing reaction path. In contrast, the results presented here suggest the predominance of the intramolecular mechanism (Scheme 7) – noteworthily in the presence of excess reducing agent. In the light of previous discussions[8] and the results presented here, the "intramolecular" twofold reduction appears to dominate with 1,3-indandiones which bear bulky groups at C-2. In

Scheme 7

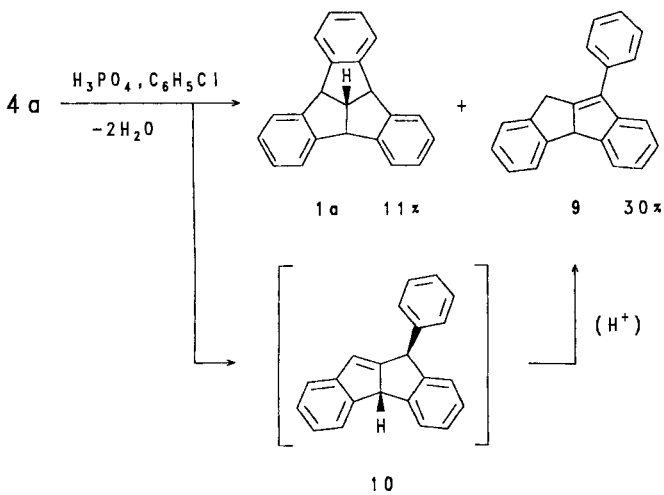


the case of the 2-benzhydryldiones **3b**, **3c**, and **3g**, the attack of a second alanate ion at the primarily formed hydridoaluminate complex **8** from the less hindered side of the second carbonyl group competes with the intramolecular transfer of a hydride at the more hindered side. In contrast, with indandiones bearing *two* bulky groups at C-2, such as **3d**–**3f**, the intermolecular attack is even more disfavored. Interestingly, 2,2-dibenzyl-1,3-indandione also undergoes exclusively the intramolecular twofold reduction[3,9a]. Thus, 2,2-dimethyl-1,3-indandione appears to be an exception rather than a representative case in showing the competition of the intra- and intermolecular reduction of nonenolizable 1,3-indandiones. Anyway, the highly dominant "steric approach control" is obvious from the fact that **3b** does not give the *all-trans*-diol **4b'**, which would require, in the first step of the reduction, attack of the alanate ion *syn* to the benzhydryl group. On the other hand, the competitive formation of *cis,trans*- and *all-cis*-**4b**, -**4c**, and -**4g** suggests that the intramolecular hydride transfer may be sterically hindered by the bulky benzhydryl group as well.

Tribenzotriquinacene

The conversion of diol **4a** into the parent tribenzotriquinacene **1a** under standard cyclodehydration conditions (H_3PO_4/toluene or xylene at reflux temperatures)[3] gives extremely low yields (1–3%). One of the side reactions found with **4a** under those conditions is the condensation of intermediate indenyl-type ions with the arene solvent[10c,17]. Therefore, we tried to suppress this reaction by using chlorobenzenes as less nucleophilic solvents. Indeed, the dehydration of **4a** with H_3PO_4/chlorobenzene at reflux temperatures furnishes an 11% yield of tribenzotriquinacene (**1a**) (Scheme 8). Fortunately, the isolation of **1a** is easy due to its extremely low solubility in apparently all organic solvents. It quantitatively precipitates as long, thin needles from the reaction mixture upon cooling. This is remarkable because the isomeric diindene **9** is formed as the main product (ca. 30% yield). As a tetrasubstituted olefin, this hydrocarbon is more stable than the isomeric olefin **10**, and is probably formed by a proton-catalyzed 1,3-H shift, instead or along with the arylation reaction. Of course, **9** cannot further cyclize to **1a**.

Scheme 8

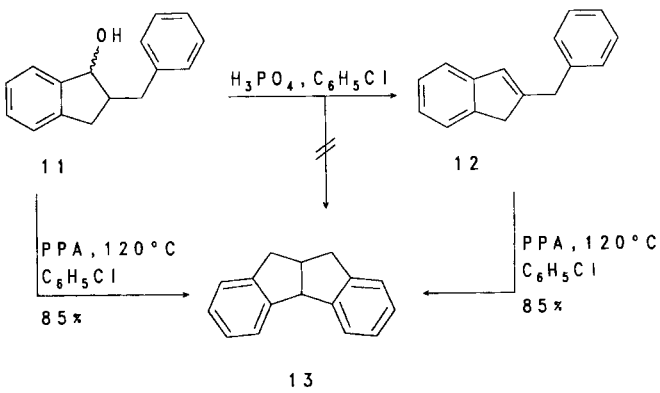


Although the 11% yield of **1a** is still unsatisfactory, the direct threestep synthesis allows the preparation of this interesting centrotriindan in gram amounts and in ca. 6% overall yield from 1,3-indandione (**2a**). It thus represents a decisive improvement of our first multistep synthesis[4,5a,25].

C_s-Diindan (Tetrahydroindeno[1,2-*a*]indene)

An interesting detail deserves to be mentioned here, because it demonstrates the difficulty in predicting the influence of the reaction parameters on cyclodehydration reactions. In the course of our attempts to improve the yield of the conversion **4a** → **1a**, we found that 2-benzyl-1-indanol (**11**) (Scheme 9) is dehydrated with H_3PO_4/chlorobenzene in good yields to the corresponding indene **12**, but not to the diindan **13**. However, at comparable temperatures (120°C), utilization of polyphosphoric acid in the same solvent produces **13** in 85% yield from both **11** and **12** as the starting materials. While the dehydration of **11** → **12** has been performed previously with differeent catalysts[26,27], the known diindan **13**[28,29] has not yet been synthesized by direct cyclodehydration. In contrast to the published procedures[28,29], the simple route presented here furnishes **13** in good yields on the 100-g scale.

Scheme 9



Of course, we tried to apply this result to the cyclodehydration of indandiol **4a**. Unfortunately, in turn, only minor yields (3%) of **1a** have been obtained under these conditions.

centro-Alkylated Tribenzotriquinacenes

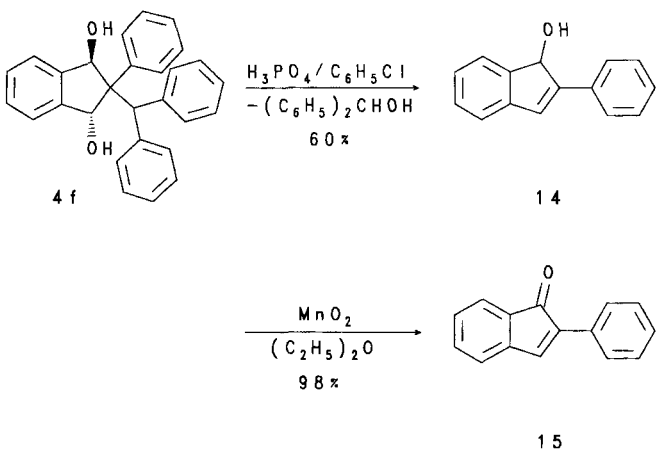
The cyclodehydration of the 2-alkyl-2-benzhydryl-1,3-indandiols **4b**–**4e** and **4g** has been achieved by utilizing H_3PO_4/xylene or toluene as the standard reaction medium. The corresponding *centro*-alkylated tribenzotriquinacenes are obtained at reflux temperatures within 2–10 h in yields of 10–33%, depending on the second substituent R. Interestingly, the yields are highest with the small substituents (R = CH_3, C_2H_5).

The tribenzotriquinacenes are identified by their simple ^{1}H- and ^{13}C-NMR spectra, which clearly reflect their C_{3v} molecular symmetry. No effects due to steric hindrance of the larger substituents (cf. **1b**, **1e**) are observed at room temperature; hence, the rotation of the benzyl and benzhydryl groups is relatively fast on the NMR time scale. There is an increasing deshielding effect of the three bridgehead protons with increasing size of the substituent, whereas the chemicals shifts of the bridgehead carbon nuclei display an inverse trend.

The mass spectra of **1a**–**1e** and **1g** reflect the stability of the positively charged tribenzotriquinacene framework. Thus, the base peaks in the 70-eV EI mass spectra of **1a** and **1b** are due to the molecular ions, and only little fragmentation is observed. With the other tribenzotriquinacenes, the loss of the alkyl substituent as a whole increases systematically with the decreasing stability of the C-*centro*–C-α bond.

The 2-phenyl- and 2-allyl-substituted indandiols (**4f** and **4g**) do not give the corresponding tribenzotriquinacenes under the conditions used here. We expected that **4f** may undergo Wagner-Meerwein rearrangement of the phenyl group as found for 2,2-diphenyl-1,3-indandiol[14], whereas **4g** would behave similarly after acid-catalyzed allyl→1-propenyl isomerization. In fact, by using the standard dehydration conditions (H_3PO_4/xylene at reflux temperatures), neither of the two diols gives the corresponding tribenzotriquinacene derivative or another well-defined product. In chlorobenzene, however, **4f** is cleaved by heterolysis of the C-2–C-α bond to give 2-phenyl-1-indenol **14** as the main product (Scheme 10). Obviously, the presence of the additional π system of the phenyl group provides a driving force for the fragmentation of **4f**. To the best of our knowledge, indenol **14** has not been described yet. It can be easily identified by NMR, IR, and MS and distinguished from the 3-phenyl isomer, which would have formed upon 1,2-phenyl shift, by oxidation to the known[30] indenone **15** with manganese dioxide. Under the same conditions, the allyl derivative **4g** undergoes C-2–C-α bond cleavage as well, but, in this case, 12d-allyltribenzotriquinacene (**1g**) is formed and can be isolated in low (10%) yield after repeated chromatography.

Scheme 10



The finding that 2-benzhydryl-1,3-indandiols bearing π substituents at C-2 do not undergo the twofold cyclodehydration is unfortunate because the synthesis of triquinacenes bearing, for example, an aryl substituent at the central carbon atom would offer an access to various interesting *centro*-functionalized triquinacene derivatives[1, 31]. Notwithstanding, the accessibility of the *centro*-alkylated tribenzotriquinacenes **1b**–**1e** and **1g** (the latter should be readily oxidizable) adds remarkably to the considerable efforts devoted to the syntheses of *centro*-alkylated triquinacenes[32,33].

Most of the tribenzotriquinacenes reported here have high melting points, as expected from their molecular shape. Thus, despite of the limited yields, **1a**, **1b**, **1d**, and **1e** can be easily isolated and purified by simple crystallization (see Experimental). However, it is instructive to note that the melting point of **1a** (390°C) is decreased by the presence of a methyl group by ca. 150°C and by an ethyl group by even ca. 240°C. These remarkably large differences are attributed to the particularly efficient stacking of these cup-shaped molecules: The X-ray structural analysis of **1b**[34] revealed that this homologue forms perfect stacks of molecules along the molecular C_{3v} symmetry axis with a translational distance of 6 Å. Whereas the removal of the methyl group allows an even closer packing in solid **1a** (probably in the same orientation), the symmetry-breaking ethyl substituent considerably weakens the intermolecular forces.

The UV spectra of the tribenzotriquinacenes **1a**–**1e** and **1g** exhibit α bands with the lowest energy transition in the range of $276.0 \leq \lambda_{max} \leq 276.8$ nm, closely corresponding to those of indan (λ_{max} = 273.2 nm)[35]. Only a slight but significant bathochromic shift has been found ($\Delta\lambda_{max}$ = 2.8–3.6 nm). Interestingly, the same effect occurs in all other higher centropolyindans which contain a tribenzotriquinacene subunit, such as trifusotetraindan (λ_{max} = 276.0 nm)[25], centropentaindan (λ_{max} = 276.0 nm)[36], and centrohexaindan (λ_{max} = 276.5 nm)[37]. This finding may suggest that the particular rigidity of the tribenzotriquinacene framework gives rise to a minor π-π hyperconjugative effect between the three adjacent aromatic systems. In contrast, isomeric centrotriindans, i.e. triptindan (λ_{max} = 273.5 nm)[38] and the angular difusotriindan (λ_{max} = 274.0 nm)[3,9a], do not exhibit this small bathochromic shift. Noteworthily, all of these centropolyindans have frameworks with a limited conformational flexibility. The same holds for 2,2-spirobiindan (λ_{max} = 274.0 nm)[39] and fenestrindan (λ_{max} = 273.5 nm)[9a,b]. The origin of the slight bathochromic shift of the α bands of the tribenzotriquinacene "chromophore" will be discussed in the context with the X-ray structural analysis of the centropolyindans[40].

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Experimental

Melting points (uncorrected): Büchi 512, Electrothermal Melting Point Apparatus (for m.p. >300°C). – IR: Perkin-Elmer 377. – UV: Beckman model 25. – ^{1}H NMR: Bruker AM 300; $CDCl_3$/

TMS. – ^{13}C NMR: Bruker AM 300 (*J*-modulated spin-echo experiments); $CDCl_3$/TMS. – MS: Finnigan MAT 311 A, Finnigan MAT CH 5 DF; EI, 70 eV. – Combustion analyses: Perkin-Elmer 240, LECO CHNS-932 Analysator. – MPLC: Kieselgel 60, 30–65 μm (LiChroprep, Merck), with Besta E 100 and Besta UV 1. – TLC: Silica gel (Kieselgel 60) on Al foil (Merck, F 254).

The 2-alkyl-1,3-indandiones **2b** and **2c** have been preprared according to a procedure described by Mosher and Soeder[41] except that toluene instead of benzene has been used as the solvent[7c]. To obtain pure material, fast workup after hydrolysis, recrystallization from methanol or ethanol, and storage of the readily air-oxidized diones at <0°C are recommended. The latter holds also for 2-benzyl-1,3-indandone (**2d**).

2,3-Dihydro-2-isopropyl-1H-indene-1,3-dione (**2h**): This compound has been prepared by analogy with Mosher and Soeder's procedure[41] by reaction of dimethyl phthalate and 2,6-dimethylheptanone (techn. grade, 70–75°C) with sodium hydride in benzene for only 3 h. After hydrolysis and workup, a red oil is obtained which may be purified by kugelrohr distillation (b.p. 160–205°C/0.3 Torr) to give a yellow, crystalline material; subsequent recrystallization from hexane gives **2h** (42.3 g, 45%) as colorless platelets, m.p. 57°C. – IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1}, 3074, 2962, 2875, 1740, 1710, 1590, 1495, 1271, 757. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.97 (2H); δ_B = 7.84 (2H)], 2.90 (d, ^3J = 3.8 Hz, 1H, 2-H), 2.58 (dq, ^3J = 3.8 Hz, ^3J = 7.0 Hz, 1H, C*H*CH_3), 1.07 (d, ^3J = 7.0 Hz, 6H, CH_3). – ^{13}C NMR (75 MHz): δ = 201.2 (q, CO), 142.8 (q), 135.5 (t), 122.8 (t), 58.5 (t, C-2), 29.3 [t, *C*H$(CH_3)_2$], 19.5 (CH_3). – MS: *m/z* (%) = 188 (24) [$M^{\cdot+}$], 173 (100), 155 (12), 146 (39), 117 (10), 115 (11), 105 (18), 104 (34).

$C_{12}H_{12}O_2$ (188.2) Ber. C 76.57 H 6.43 Gef. C 76.86 H 6.43

2-(Diphenylmethyl)-2,3-dihydro-2-methyl-1H-indene-1,3-dione (**3b**): A solution of 80.0 g (500 mmol) of 2-methyl-1,3-indandione (**2b**), 92.0 g (500 mmol) of diphenylmethanol, and 4.9 g (25 mmol) of *p*-toluenesulfonic acid (PTSA) monohydrate in 600 ml of benzene is heated to reflux in a reaction apparatus equipped with a water separator. After 2 h, the water has been separated quantitatively, and the solvent is evaporated. The residue is dissolved in 300 ml of chloroform, and the solution is washed with 5% aqueous Na_2CO_3 and then with water. After drying with Na_2SO_4, the solvent is evaporated to give a highly concentrated, hot solution (ca. 100 ml), from which, upon addition of methanol, pure diketone **3b** precipitates (147 g, 90%) as colorless needles; m.p. 122°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 1730, 1695, 1582, 1480, 1260, 1235, 695. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.80 (2H); δ_B = 7.68 (2H)], 7.44 (d, ^3J = 7.9 Hz, 4H), 7.15 (t, ^3J = 7.7 Hz, 4H), 7.06 (t, ^3J = 7.3 Hz, 2H), 4.56 (s, 1H, $CHPh_2$), 1.28 (s, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 204.2 (q, CO), 141.4 (q), 139.7 (q), 135.5 (t), 129.7 (t), 128.2 (t), 126.7 (t), 123.0 (t), 58.2 (q, C-2), 57.9 (t, $CHPh_2$), 19.9 (CH_3). – MS: *m/z* (%) = 326 (1.3) [$M^{\cdot+}$], 167 (100) [$CHPh_2^+$], 165 (12), 115 (3).

$C_{23}H_{18}O_2$ (326.4) Ber. 84.64 H 5.56 Gef. C 84.55 H 5.76

2-(Diphenylmethyl)-2-ethyl-2,3-dihydro-1H-indene-1,3-dione (**3c**): In a reaction apparatus equipped with a water separator, a solution of 34.8 g (200 mmol) of **2c**, 36.8 g (200 mmol) of diphenylmethanol, and 1.94 g (10.0 mmol) of PTSA in 500 ml of benzene is heated to reflux for 5 h. After the water has been separated completely, the solvent is evaporated, and the residue is dissolved in 250 ml of chloroform. The solution obtained is washed with 5% aqueous Na_2CO_3. After drying with Na_2SO_4 and evaporation of the solvent, the bright-yellow product is recrystallized from ethanol to give **3c** (61.9 g, 91%) as colorless needles; m.p. 92°C. – IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 3030, 2968, 2935, 1740, 1700, 1592, 1495, 1449, 1245. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.81 (2H); δ_B = 7.66 (2H)], 7.45 (d, ^3J = 7.3 Hz, 4H), 7.17–7.12 (m, 4H), 7.03–7.08 (m, 2H), 4.53 (s, 1H, $CHPh_2$), 1.92 (q, ^3J = 7.5 Hz, 2H, CH_2), 0.58 (t, ^3J = 7.5 Hz, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 204.5 (q, CO), 142.9 (q), 139.7 (q), 135.2 (t), 129.6 (t), 128.2 (t), 126.6 (t), 122.4 (t), 63.3 (q), 58.1 (t, $CHPh_2$), 27.8 (s, CH_2), 9.2 (CH_3). – MS: *m/z* (%) = 340 (0.4) [$M^{\cdot+}$], 311 (0.8) [$M^{\cdot+}$ – C_2H_5], 167 (100) [$CHPh_2^+$], 165 (20), 152 (14), 115 (5), 91 (5).

$C_{24}H_{20}O_2$ (340.4) Ber. C 84.68 H 5.92 Gef. C 84.36 H 5.99

2-Benzyl-2-(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-dione (**3d**): In a reaction apparatus equipped with a Soxhlet extractor filled with 60 g of molecular sieves (4 Å), a solution of 23.6 (100 mmol) of **2d**, 18.4 g (100 mmol) of diphenylmethanol, and 1.90 g (10.0 mmol) of PTSA in 400 ml of benzene is heated under reflux for 18 h. The solvent is evaporated under reduced pressure, and the light-brown residue is dissolved in 400 ml of $CHCl_3$. The solution is washed with 5% aqueous Na_2CO_3 and then with water and dried with Na_2SO_4; the solvent is evaporated, and the residue is recrystallized from a mixture of methanol and $CHCl_3$ (3:1, v/v) to give **3d** (35.5 g, 88.1%); m.p. 146°C. – IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1}, 3010, 1725, 1690, 1580, 1485, 1445, 1240, 745, 690. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.57 (2H); δ_B = 7.45 (2H)], 7.52 (d, ^3J = 7.3 Hz, 4H), 7.17 (t, ^3J = 7.4 Hz, 4H), 7.06 (t, ^3J = 7.4 Hz, 2H), 6.86–6.92 (m, 5H), 4.68 (s, 1H, $CHPh_2$), 3.15 (s, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 203.8 (q, CO), 142.9 (q), 139.5 (q), 135.4 (q), 135.0 (t), 130.0 (t), 129.8 (t), 128.3 (t), 127.8 (t), 126.8 (t), 126.5 (t), 122.2 (t), 64.5 (q, C-2), 58.5 (t, $CHPh_2$), 40.9 (s, CH_2). – MS: *m/z* (%) = 402 (1) [$M^{\cdot+}$], 311 (1) [$M^{\cdot+}$ – $C_6H_5CH_2$], 233 (1), 167 (100) [$CHPh_2^+$], 165 (19), 152 (10), 91 (7), 77 (3).

$C_{29}H_{22}O_2$ (402.5) Ber. C 86.54 H 5.51 Gef. C 86.26 H 5.42

2,2-Bis(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-dione (**3e**): In a reaction apparatus equipped with a water separator, a solution of 77.3 g (500 mmol) of **2a**, 188 g (1.02 mol) of diphenylmethanol, and 19.6 g (100 mmol) of PTSA in 2.0 l of benzene is heated to reflux. After the water has been separated completely (<15 h), the solvent is evaporated, and the residue is dissolved in chloroform. The solution is washed trice with 5% aqueous Na_2CO_3 and then with water and dried with Na_2SO_4. After evaporation of most of the solvent, methanol is added to precipitate the product, which is then filtered by suction and washed with some methanol. Recrystallization from methanol gives **3e** as an almost colorless powder (181 g, 76.0%); m.p. 199–200°C (ref.[18] 205–207°C). – IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 3065, 3031, 2926, 1736, 1702, 1493, 1450, 1242, 1030, 772, 700. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.57 (2H); δ_B = 7.43 (2H)], 7.30 (d, ^3J = 8.1 Hz, 8H), 6.90–7.13 (m, 12H), 4.83 (s, 2H, $CHPh_2$). – ^{13}C NMR (75 MHz): δ = 204.1 (q, CO), 142.7 (q), 139.4 (q), 134.9 (t), 129.9 (t), 127.9 (t), 126.3 (t), 122.2 (t), 67.2 (q, C-2), 56.5 (t, $CHPh_2$). – MS: *m/z* (%) = 478 (3) [$M^{\cdot+}$], 311 (13), 310 (5), 309 (5), 265 (10), 252 (11), 233 (16), 168 (45), 167 (100), 166 (35), 165 (42), 152 (39).

2-(Diphenylmethyl)-2,3-dihydro-2-phenyl-1H-indene-1,3-dione (**3f**) was obtained as described in the literature[18]; m.p. 199–201°C (ref.[18] 200–200.5°C). – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3028, 3007, 1741, 1702, 1494, 1451, 1256, 1035, 774, 695, 627. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.85 (2H); δ_B = 7.68 (2H)], 7.35 (d, ^3J = 8.5 Hz, 2H), 7.31 (t, ^3J = 7.4 Hz, 4H), 6.95–7.18 (m, 9H), 5.37 (s, 1H, $CHPh_2$). – ^{13}C NMR (75 MHz): δ = 201.0 (q, CO), 141.7 (q), 139.7 (q), 135.7 (q), 135.6 (t), 130.3 (t), 128.3 (t), 127.9 (t), 127.4 (t), 126.4 (t), 123.4 (t), 66.8 (q, C-2), 57.5 (t, $CHPh_2$). – MS: *m/z* (%) = 167 (100) [$CHPh_2^+$], 165 (19), 152 (11), 115 (1), 77 (2).

2-Allyl-2-(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-dione (**3g**): To a stirred solution of 15.5 g (50 mmol) of **2e** in 150 ml of ace-

tonitrile is added 60 g of KF/Celite (50% KF w/w)[21] and then 13.5 ml (80 mmol) of freshly distilled allyl iodide. Stirring is continued while the mixture is heated to 70°C for 4 h. After cooling, the solution is filtered, and the residue is washed twice with THF. The solutions are combined, and the solvents are evaporated to give an oily residue. Recrystallization from ethanol yields 14.4 g (82%) of **3g** as a colorless powder; m.p. 129°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3025, 3005, 2975, 2950, 2900, 2850, 1730, 1693, 1630, 1588, 1240, 920, 770, 700. – ^1H NMR (300 MHz): AA'BB' spin system [δ_A = 7.77 (2H); δ_B = 7.62 (2H)], 7.44–7.48 (d, ^3J = 8.7 Hz, 4H), 7.00–7.17 (m, 6H), 5.26–5.35 (m, 1H, C*H*CH_2), 4.90 [dq, ^3J = 17.0 Hz, 1H, (*E*)-CHCH*H*], 4.75 [dd, ^3J = 10.2 Hz, 1H, (*Z*)-CHCH*H*], 4.56 (s, 1H, $CHPh_2$), 2.60 (d, ^3J = 7.5 Hz, 2H, $CH_2CH{=}CH_2$). – ^{13}C NMR (75 MHz): δ = 203.7 (q, CO), 142.7 (q), 139.3 (q), 135.4 (t), 131.3 (t), 129.6 (t), 128.2 (t), 126.8 (t), 122.6 (t), 119.6 (s), 62.7 (q, C-2), 58.0 (t, $CHPh_2$), 38.9 (s, CH_2). – MS: *m/z* (%) = 352 (3) [$M^{\cdot+}$], 311 (1), 167 (100), 165 (13), 152 (9), 128 (2), 77 (3).

$C_{25}H_{20}O_2$ (352.4) Ber. C 85.20 H 5.72 Gef. C 85.09 H 5.79

2,3-Dihydro-2-(triphenylmethyl)-1H-indene-1,3-dione (**3i**): A solution of 14.6 g (100 mmol) of **2a**, 24.8 g (100 mmol) of triphenylmethanol, and 1.70 g (10.0 mmol) of PTSA in 500 ml of anhydrous benzene is heated under reflux for 40 h in a Soxhlet extractor filled with 25 g of molecular sieves (4 Å). The deeply red-brown reaction mixture is allowed to cool while the major part of **3i** precipitates as needles, which are filtered by suction. The filtrate is concentrated to dryness and redissolved in CH_2Cl_2; the solution is washed twice with 5% aqueous Na_2CO_3 and then with water and dried with Na_2SO_4. The solvent is removed, and the residue is combined with the precipitated product and recrystallized from EtOAc/MeOH (4:1) to give 24.1 g (62%) of **3i**; m.p. 237°C (ref.[19] 231–234°C). – IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3065, 3030, 2920, 1740, 1705, 1587, 1255, 765, 735, 700. – ^1H NMR (300 MHz): δ = 7.59 (m, 4H), 7.35 (br. d, ^3J = 7.4 Hz, 6H), 7.16 (br. t, ^3J = 7.3 Hz, 6H), 7.08 (br. t, ^3J = 7.1 Hz, 4H), 4.90 (s, 1H, 2-H). – ^{13}C NMR (75 MHz): δ = 198.5 (q, CO), 143.7 (q), 142.7 (q), 134.9 (t), 129.5 (t), 127.5 (t), 126.3 (t), 122.5 (t), 61.3 (q, CPh_3), 56.8 (t, C-2). – MS: *m/z* (%) = 388 (5) [$M^{\cdot+}$], 243 (100) [CPh_3^+], 178 (11), 165 (81), 104 (10), 77 (10), 76 (13).

all-cis-2-(Diphenylmethyl)-2,3-dihydro-1H-indene-1,3-diol (**4a**): To a solution of 31.2 g (100 mmol) of **3a** in 300 ml of ethyl acetate is added 50 g of Urushibara nickel[42]. The suspension is shaken under hydrogen (1 bar) at room temp. until 2 equiv. of gas have reacted (ca. 1 d), while the solution decolorizes and the diol crystallizes in part. The solution is heated to 50–60°C, and the pyrophoric catalyst (***Caution!***) is removed by careful filtration of the hot solution; the diol **4a** precipitates upon cooling and may be recrystallized to give colorless needles from ethanol (16–22 g, 50–70%); m.p. 202°C. [The mother liquor contains the corresponding ketol, *2-(diphenylmethyl-2,3-dihydro-1H-inden-1-ol-3-one*; reduction at 2 bar H_2 or for prolonged reaction times gives *2-(diphenylmethyl)-2,3-dihydro-1H-indene*]. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (br.), 3063, 3029, 1492, 1450, 1035. – ^1H NMR (300 MHz): δ = 7.50 (d, ^3J = 7.7 Hz, 4H), AA'BB' spin system [δ_A = 7.41 (2H); δ_B = 7.34 (2H)], 7.35 (d, ^3J = 7.7 Hz, 4H), 7.23 (d, ^3J = 7.4 Hz, 2H), 4.80 (dt, ^3J = 6.3 Hz, ^3J = 5 Hz, 2H, C*H*OH), 4.61 (d, ^3J = 12.2 Hz, 1H, $CHPh_2$), 3.04 (dt, ^3J = 12.2 Hz, ^3J = 4.5 Hz), 2.06 (d, ^3J = 6.3 Hz, 2H, OH). – ^{13}C NMR (75 MHz): δ = 145.1 (q), 143.1 (q), 129.2 (t), 128.7 (t), 128.2 (t), 126.2 (t), 125.4 (t), 75.0 (t), 53.0 (t), 47.2 (t). – MS: *m/z* (%) = 316 (1) [$M^{\cdot+}$], 298 (6), [$M^{\cdot+}$ – H_2O], 280 (31) [$M^{\cdot+}$ – 2 H_2O], 167 (100) [$CHPh_2^+$], 165 (21), 131 (45), 118 (75).

$C_{22}H_{20}O_2$ (316.4) Ber. C 83.52 H 6.37 Gef. C 83.55 H 6.36

all-cis- and cis,trans-2-(Diphenylmethyl)-2,3-dihydro-2-methyl-1H-indene-1,3-diol (*all-cis*-**4b** and *cis,trans*-**4b**): A solution of 163 g (500 mmol) of **3b** in 250 ml of anhydrous THF is added through a dropping funnel to a magnetically stirred suspension of 19.0 g (500 mmol) of $LiAlH_4$ in 250 ml of THF. The mixture is heated under reflux for 3 h and then concentrated by distillation of the major part (ca. 350 ml) of the solvent. After cooling to room temp. and addition of 300 ml of diethyl ether, the mixture is carefully (!) hydrolyzed by the addition of small pieces of ice. The organic layer is decanted as far as possible from the aluminum salts, the salts are washed once with THF/diethyl ether, and the organic solutions are combined. Complete evaporation of the solvents affords a yellow oily residue which contains a mixture of *all-cis*-**4b** and *cis,trans*-**4b** (>92% yield) in a ratio of 26:74 (^1H-NMR); it may be used without further purification in the cyclodehydration step. Fractional recrystallization from methanol gives first *all-cis*-**4b** as a colorless powder (36.1 g, 22%); m.p. 191–192°C. Then *cis,trans*-**4b** is obtained as a colorless powder (98.3 g, 60%); m.p. 70–73°C).

all-cis-**4b**: IR (KBr): $\tilde{\nu}$ = 3433 cm^{-1}, 3263 (br.), 3059, 3027, 2992, 2964, 2917, 1494, 1446, 1412, 1006, 760, 714. – ^1H NMR (300 MHz): δ = 7.56 (d, ^3J = 8.0 Hz, 4H), AA'BB' spin system [δ_A = 7.42 (2H); δ_B = 7.35 (overlapped, 2H)], 7.34 (t, ^3J = 8 Hz, 4H), 7.24 (t, ^3J = 7.5 Hz, 2H), 5.23 (s, 1H, $CHPh_2$), 4.55 (d, ^3J = 7.2 Hz, 2H, C*H*OH), 2.25 (d, ^3J = 7.3 Hz, 2H, OH), 0.84 (s, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 144.7 (q), 141.9 (q), 129.9 (t), 129.1 (t), 128.5 (t), 126.4 (t), 126.1 (t), 81.7 (t, CHOH), 53.4 (q, C-2), 48.8 (t, $CHPh_2$), 20.5 (CH_3). – MS: *m/z* (%) = 330 (1) [$M^{\cdot+}$], 312 (3) [$M^{\cdot+}$ – H_2O], 294 (14) [$M^{\cdot+}$ – 2 H_2O], 279 (2), 167 (100), 165 (24), 145 (69), 115 (16), 91 (22), 77 (14).

$C_{23}H_{22}O_2$ (330.4) Ber. C 83.60 H 6.71 Gef. C 83.87 H 6.72

cis,trans-**4b**: IR (KBr): $\tilde{\nu}$ = 3578 cm^{-1}, 3452 (br.), 3063, 3031, 3003, 2967, 2903, 1493, 1448, 1384, 1051, 1016, 772, 711. – ^1H NMR (300 MHz): δ = 7.64 (d, ^3J = 8.1 Hz, 2H), 7.57 (d, ^3J = 8.8 Hz, 2H), 7.20–7.40 (m, 10H), 5.48 (d, ^3J = 3.8 Hz, 1H, C*H*OH), 4.88 (d, ^3J = 4.2 Hz, 1H, $CHPh_2$), 4.74 (br. d, $^3J \approx$ 2.9 Hz, 1H, C*H*OH), 1.75 (br. d, $^3J \approx$ 3.7 Hz, 1H, OH), 1.09 (s, 3H, CH_3), 0.99 (d, ^3J = 4.2 Hz, 1H, OH). The assignment of the signals given in Scheme 6 is corroborated by selective decoupling of the carbinol and hydroxy protons. – ^{13}C NMR (75 MHz): δ = 144.1 (q), 142.5 (q), 142.0 (q), 141.0 (q), 130.0 (t), 129.7 (t), 129.2 (t), 128.8 (t), 128.4 (t), 128.1 (t), 127.0 (t), 126.4 (t), 125.0 (t), 124.6 (t), 81.0 (t, CHOH), 80.8 (t, CHOH), 55.6 (q, C-2), 55.1 (t, $CHPh_2$), 15.2 (CH_3). – MS: *m/z* (%) = 312 (3) [$M^{\cdot+}$ – H_2O], 294 (2), 279 (4), 167 (100) [$CHPh_2^+$], 165 (30), 145 (36), 117 (28), 115 (33), 91 (31), 77 (22).

$C_{23}H_{22}O_2$ (330.4) Ber. C 83.60 H 6.71 Gef. C 83.55 H 6.66

all-cis- and cis,trans-2-(Diphenylmethyl)-2-ethyl-2,3-dihydro-1H-indene-1,3-diol (*cis,trans*-**4c** and *all-cis*-**4c**): A suspension of 2.30 g (60.0 mmol) of $LiAlH_4$ in 300 ml of anhydrous THF is stirred while a solution of 34.0 g (100 mmol) of **3c** in 250 ml of THF is added through a dropping funnel. The mixture is heated under reflux for 3 h, cooled, carefully hydrolyzed with small pieces of ice, and filtered by suction. The filtrate is concentrated to dryness by evaporation of the solvent. The yellow residue (crude yield 88%) contains *all-cis*-**4c** and *cis,trans*-**4c** in a ratio of 30:70 (^1H NMR), which are separated by fractionated recrystallization from ethanol. The first fraction consists of a colorless powder, *all-cis*-**4c** (9.40 g, 29%); m.p. 166°C (from CH_2Cl_2/MeOH). The residual material gives, after recrystallization from $CHCl_3$, *cis,trans*-**4c** as a colorless powder (20.3 g, 59%); m.p. 122°C.

all-cis-**4c**: IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1}, 3293 (br.), 3054, 3025, 2982, 2914, 1597, 1493, 1446, 1208, 1031. – ^1H NMR (300 MHz): δ = 7.57 (d, ^3J = 8.6 Hz, 4H), AA'BB' spin system [δ_A = 7.45 (2H);

δ_B = 7.35 (partially overlapped, 2H)], 7.37–7.32 (m, 4H), 7.22–7.28 (m, 2H), 5.33 (s, 1H, $CHPh_2$), 4.75 (d, ^3J = 7.1 Hz, 2H, *CH*OH), 2.27 (d, ^3J = 7.2 Hz, 2H, OH), 1.61 (q, ^3J = 7.7 Hz, 2H, CH_2), −0.02 (t, ^3J = 7.7 Hz, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 144.9 (q), 142.1 (q), 129.9 (t), 129.3 (t), 128.5 (t), 126.4 (t), 125.4 (t), 80.2 (t), 55.1 (q), 48.9 (t), 26.8 (s), 10.0. – MS: *m/z* (%) = 326 (4) [$M^{\bullet+}$ – H_2O], 308 (8) [$M^{\bullet+}$ – 2 H_2O], 279 (4), 177 (5), 167 (100) [$CHPh_2^+$], 160 (28), 159 (35), 131 (8), 118 (6), 91 (10).

$C_{24}H_{24}O_2$ (344.5) Ber. C 83.69 H 7.02 Gef. C 83.02 H 6.74

cis,trans-**4c**: IR (KBr): $\tilde{\nu}$ = 3542 cm^{-1}, 3402 (br.), 3064, 2986, 2974, 2944, 2878, 1494, 1462, 1449, 1180, 1064, 1011, 756, 647. – ^{1}H NMR (300 MHz): δ = 7.58 (d, ^3J = 7.6 Hz, 2H), 7.51 (d, ^3J = 7.7 Hz, 2H), 7.17–7.36 (m, 10H), 5.50 (d, ^3J = 4.5 Hz, 1H, *CH*OH), 5.12 (d, ^3J = 4.0 Hz, 1H, *CH*OH), 4.88 (s, 1H, $CHPh_2$), 1.94 (d-AB, ^2J = −14.7 Hz, ^3J = 7.5 Hz, 2H, CH_2), 1.78 (d, ^3J = 4.3 Hz, 1H, OH), 1.13 (d, ^3J = 4.7 Hz, 1H, OH), 0.31 (t, ^3J = 7.6 Hz, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 144.8 (q), 142.8 (q), 142.5 (q), 141.7 (q), 130.4 (t), 129.8 (t), 129.1 (t), 128.6 (t), 128.2 (t), 126.8 (t), 126.1 (t), 123.9 (t), 123.2 (t), 80.6 (t), 79.3 (t), 56.9 (q), 55.6 (t), 23.3 (s), 10.7. – MS: *m/z* (%) = 326 (1) [$M^{\bullet+}$ – H_2O], 279 (2), 167 (100) [$CHPh_2^+$], 165 (14), 160 (5), 159 (15), 91 (14).

$C_{24}H_{24}O_2$ (344.5) Ber. C 83.69 H 7.02 Gef. C 83.49 H 6.96

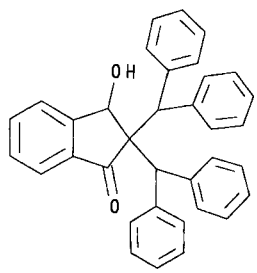
cis,trans-2-Benzyl-2-(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-diol (**4d**): A suspension of 4.80 g (125 mmol) of $LiAlH_4$ in 250 ml of anhydrous THF is stirred while a solution of 40.2 g (100 mmol) of **3d** in 200 ml of THF is added through a dropping funnel. The mixture is heated under reflux until the reaction is completed [< 3 h as monitored by TLC (CH_2Cl_2)]. The major portion (ca. 350 ml) of the solvent is distilled off and replaced by ca. 300 ml of diethyl ether. The mixture is carefully (!) hydrolyzed with ice/water, the organic solution is separated, and the inorganic products are extracted several times with diethyl ether. The combined organic solutions are washed with water and dried with Na_2SO_4, the solvent is evaporated, and the viscous residue is recrystallized from ca. 50 ml of methanol/CH_2Cl_2 (3:1, v/v) to give **4d** (32.5 g, 80.0%) as a colorless solid; m.p. 86°C. – IR (KBr): $\tilde{\nu}$ = 3560 cm^{-1}, 3440 (br.), 3050, 3020, 2920, 1590, 760, 750, 700. – ^{1}H NMR (300 MHz): δ = 7.69 (d, ^3J = 7.5 Hz, 2H), 7.55 (d, ^3J = 7.0 Hz, 2H), 7.24–7.42 (m, 6H), 7.10–7.20 (m, 2H), 6.90 (t, ^3J = 6.8 Hz, 1H), 6.80 (m, 3H), 6.66 (quasi-d, ^3J = 7.7 Hz, 3H), 5.61 (d, ^3J = 4.2 Hz, 1H, *CH*OH), 5.13 (d, ^3J = 4.3 Hz, 1H, *CH*OH), 5.04 (s, 1H, $CHPh_2$), AB spin system [δ_A = 3.35; δ_B = 3.21 (^2J = −13.5 Hz, 2H, CH_2)], 1.56 (d, ^3J = 4.6 Hz, 1H, OH), 1.23 (d, ^3J = 4.3 Hz, 1H, OH). – ^{13}C NMR (75 MHz): δ = 144.1 (q), 142.6 (q), 142.4 (q), 141.5 (q), 138.2 (q), 130.6 (t), 129.7 (t), 128.8 (t), 128.4 (t), 127.8 (t), 127.0 (t), 126.8 (t), 126.3 (t), 125.0 (t), 123.7 (t), 123.2 (t), 80.8 (t, CHOH), 78.4 (t, CHOH), 58.5 (q, C-2), 55.2 (t, $CHPh_2$), 33.9 (s, CH_2Ph). – MS: *m/z* (%) = 406 (1) [$M^{\bullet+}$], 388 (3) [$M^{\bullet+}$ – H_2O], 370 (3) [$M^{\bullet+}$ – 2 H_2O], 314 (12), 297 (8), 279 (3), 239 (10), 221 (40), 168 (45), 167 (100) [$CHPh_2^+$], 165 (19), 152 (11), 147 (30), 91 (69).

$C_{29}H_{26}O_2$ (406.5) Ber. C 85.68 H 6.45 Gef. C 85.41 H 6.57

cis,trans-2,2-Bis(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-diol (**4e**): A suspension of 17.5 g (462 mmol) of $LiAlH_4$ in 1.0 l of anhydrous THF is vigorously stirred while a solution of 50.0 g (105 mmol) of **3e** in 400 ml of THF is slowly added through a dropping funnel. The mixture is heated under reflux until the starting material has reacted completely [ca. 1 d, as controlled by TLC (CH_2Cl_2)]. The major portion (ca. 700 ml) of the solvent is distilled off and replaced by ca. 500 ml of diethyl ether (the solubility of the product in this solvent is very low). The mixture is carefully (!) hydrolyzed with small pieces of ice and then with a total of 1 l of water, and the solid material thus formed is filtered off by suction with a sintered-glass filter. The inorganic components are extracted by repeated digestion of the mixture with dilute (30%) sulfuric acid and removal of the acidic solution by suction through the sintered-glass filter. After neutralization by washing with water, the material is extracted in a Soxhlet extractor with 600 ml of hot THF. The *trans*-diol **4e** crystallizes in fine, white needles (43.0 g, 85%); m.p. 265°C. The diol cocrystallizes with ca. 1 equiv. of THF (^{1}H NMR). – IR (KBr): $\tilde{\nu}$ = 3550 cm^{-1}, 3420 (br.), 3060, 3030, 2980, 1600, 1585, 1490, 1450, 760, 740, 710 (br.). – ^{1}H NMR (300 MHz): δ = 7.31 (d, ^3J = 7.8 Hz, 4H), 7.26 (d, ^3J = 8.0 Hz, 4H), 6.88–7.05 (m, 16H), 6.17 (d, ^3J = 8.7 Hz, 2H, *CH*OH), 4.92 (s, 2H, $CHPh_2$), 1.94 (br. d, ^3J = 9.0 Hz, 2H, OH). – ^{13}C NMR (75 MHz): δ = 143.1 (q), 143.0 (q), 131.1 (t), 130.2 (t), 128.4 (t), 127.8 (t), 125.8 (t), 125.4 (t), 123.3 (t), 79.9 (t, CHOH), 59.2 (q, C-2), 56.4 (t, $CHPh_2$). – MS: *m/z* (%) = 464 (0.8) [$M^{\bullet+}$ – H_2O], 446 (0.6) [$M^{\bullet+}$ – 2 H_2O], 297 (24) [$M^{\bullet+}$ – H_2O – $CHPh_2$], 219 (15), 191 (9), 167 (100) [$CHPh_2^+$], 165 (39), 152 (26), 91 (19). – An analytically pure sample is obtained by recrystallization from ethanol or toluene.

$C_{35}H_{30}O_2$ (482.6) Ber. C 87.10 H 6.27 Gef. C 87.25 H 6.27

2-Bis(diphenylmethyl)-2,3-dihydro-1-hydroxy-1H-inden-3-one (**4e''**): This compound is obtained in varied amounts (e.g. 30% yield) by incomplete reduction of **3e** (e.g. after a reaction time of only 4 h); it is separated from **4e** by fractional recrystallization from ethanol to give a colorless powder; m.p. 229°C. – IR (KBr): $\tilde{\nu}$ = 3490 cm^{-1} (br.), 3070, 3030, 3010, 2890, 1690, 1600, 770, 750, 710 (br.). – ^{1}H NMR (300 MHz): δ = 7.63 (d, ^3J = 7.6 Hz, 1H), 7.05–7.43 (m, 17H), 6.99 (t, 7.5 Hz, 2H), 6.78–6.94 (m, 4H), 5.90 (d, ^3J = 11.1 Hz, 1H, *CH*OH), 5.02 (s, 1H, $CHPh_2$), 4.86 (s, 1H, $CHPh_2$), 2.29 (d, ^3J = 11.2 Hz, 1H, OH). – ^{13}C NMR (75 MHz): δ = 207.0 (q, CO), 153.8 (q), 141.7 (q), 141.0 (q), 140.7 (q), 140.3 (q), 136.9 (q), 135.0 (t), 131.0 (t), 130.6 (q), 130.3 (t), 129.6 (t), 128.9 (t), 128.6 (t), 128.3 (t), 127.9 (t), 127.6 (t), 126.4 (t), 126.2 (t), 124.1 (t), 122.7 (t), 74.0 (t, CHOH), 63.8 (q, C-2), 55.8 (t, $CHPh_2$), 55.4 (t, $CHPh_2$). – MS: *m/z* (%) = 480 (0.6) [$M^{\bullet+}$], 313 (6) [$M^{\bullet+}$ – $CHPh_2$], 296 (6), 295 (4), 265 (2), 235 (2), 168 (27), 167 (100) [$CHPh_2^+$], 165 (17), 152 (10).



4 e ''

cis,trans-2-(Diphenylmethyl)-2,3-dihydro-2-phenyl-1H-indene-1,3-diol (**4f**): A suspension of 7.00 g (184 mmol) of $LiAlH_4$ in 350 ml of anhydrous THF is stirred while a solution of 67.0 g (172 mmol) of **3f** in 600 ml of THF is added through a dropping funnel. The mixture is heated under reflux until the starting material has vanished [ca. 2 d, as monitored by TLC (CH_2Cl_2)]. The major portion (ca. 700 ml) of the solvent is distilled off, and the mixture is hydrolyzed by careful (!) addition of small pieces of ice and then 700 ml of water. This mixture is extracted with diethyl ether in a Kutscher-Steudel extractor for 50 h, the extract is washed with water and dried with Na_2SO_4, and the solvent is evaporated almost completely to give a foamy residue, which is crystallized from methanol/ethyl acetate to give **4f** as colorless powder (53.5 g, 78.0%); m.p.

179°C. – IR (KBr): $\tilde{\nu}$ = 3520 cm^{-1}, 3480, 3440 (br.), 3320 (br.), 3020, 2965, 2900, 1585, 1570, 1480, 755, 750, 690. – ^1H NMR (300 MHz): δ = 7.40–7.52 (m, 4H), 7.38 (s, 5H, 2-Ph), 7.19 (m, 3H), 7.13 (m, 3H), 6.98–7.01 (m, 2H), 6.80–6.83 (m, 2H), 5.85 (d, ^3J = 9.9 Hz, 1H, C*H*OH), 5.31 (br. s, 1H, C*H*OH), 4.30 (s, 1H, $CHPh_2$), 1.82 (d, ^3J = 10.1 Hz, 1H, OH), 1.55 (br. s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 144.9 (q), 141.8 (q), 140.6 (q), 140.5 (q), 139.7 (q), 130.7 (t), 129.9 (t), 129.3 (t), 128.5 (t), 128.4 (t), 127.8 (t), 127.1 (t), 126.8 (t), 126.7 (t), 125.1 (t), 123.9 (t), 81.9 (t, CHOH), 78.5 (t, CHOH), 64.5 (q, C-2), 55.1 (t, $CHPh_2$). – MS: *m/z* (%) = 365 (2), 224 (21) [$M^{\cdot+}$ – CH_2Ph_2], 208 (20), 207 (28) [$M^{\cdot+}$ – ($CHPh_2$, H_2O)], 179 (29), 178 (34), 168 (16), 167 (100) [$CHPh_2^+$], 152 (19), 105 (8), 91 (10), 77 (14).

$C_{28}H_{24}O_2$ (392.5) Ber. C 85.68 H 6.16 Gef. C 85.50 H 6.39

all-cis- and cis,trans-2-Allyl-2-(diphenylmethyl)-2,3-dihydro-1H-indene-1,3-diol (*all-cis*-**4g** and *cis,trans*-**4g**): To a stirred suspension of 1.65 g (30 mmol) of $LiAlH_4$ in 150 ml of anhydrous THF is added a solution of 17.5 g (50 mmol) of **3g** in 100 ml of THF. The mixture is heated under reflux for 3 h, cooled, and treated carefully with small pieces of ice until complete hydrolysis has just been achieved. The organic layer is separated, the pasty hydroxides are digested with THF, and the combined solutions are concentrated to dryness by evaporation. The yellow residue (crude yield 1.42 g, 86%) contains *all-cis*-**4g** and *cis,trans*-**4g** in a ratio of 31:69 (^1H NMR). The isomers are separated by fractional crystallization from methanol/water (ca. 80:20, v/v) to give *all-cis*-**4g** (0.41 g, 25%) as the first fraction (colorless powder); m.p. 150°C ($MeOH/H_2O$). The mother liquor gives an oil, which is dissolved in *n*-heptane to give *cis,trans*-**4g** as colorless crystals (0.96 g, 58%); m.p. 119°C.

all-cis-**4g**: IR (KBr): $\tilde{\nu}$ = 3336 cm^{-1} (br.), 3056, 3029, 2980, 2935, 1495, 1448, 1431, 1005, 755, 702. – ^1H NMR (300 MHz): δ = 7.55 (d, ^3J = 7.2 Hz, 4H), 7.26–7.42 (m, 10H), 5.34 (s, 1H, $CHPh_2$), 4.73 (s, 2H, C*H*OH), 4.23–4.48 (m, 3H, CH=CH_2), 2.18–2.34 (m, 4H, CH_2 and OH). – ^{13}C NMR (75 MHz): δ = 144.5 (q), 141.9 (q), 134.1 (t), 129.9 (t), 129.2 (t), 128.6 (t), 126.5 (t), 125.5 (t), 116.6 (s), 80.5 (t, CHOH), 55.8 (q, C-2), 48.8 (t, $CHPh_2$), 38.9 (s, CH_2). – MS: *m/z* (%) = 320 (4) [$M^{\cdot+}$ – 2 H_2O], 297 (4) [$M^{\cdot+}$ – (H_2O, C_3H_5)], 279 (5), 219 (3), 171 (26), 167 (100) [$CHPh_2^+$], 165 (15), 152 (10), 91 (10).

$C_{25}H_{24}O_2$ (356.5) Ber. C 84.24 H 6.79 Gef. C 83.87 H 6.91

cis,trans-**4g**: IR (KBr): $\tilde{\nu}$ = 3569 cm^{-1}, 3441 (br.), 3069, 3025, 2975, 2917, 1493, 1448, 1176, 1028, 906, 763, 711. – ^1H NMR (300 MHz): δ = 7.62 (d, 2H, ^3J = 7.6 Hz), 7.53 (d, 2H, ^3J = 7.8 Hz), 7.20–7.38 (m, 10H), 5.56 (d, ^3J = 5.7 Hz, 1H, C*H*OH), 5.13 (d, ^3J = 5.2 Hz, 1H, C*H*OH), 5.03–5.13 (m, 1H, C*H*=CH_2), 4.90 (s, 1H, C*H*Ph_2), 4.76 [dq, ^3J = 16.4 Hz, 1H, (*E*)-C=CH*H*], 4.55 [dd, 1H, ^3J = 9.9 Hz, (*Z*)-C=CH*H*], 2.62 (quasi-d, ^3J = 6.7 Hz, 2H, CH_2CH=CH_2), 1.65 (d, ^3J = 5.3 Hz, 1H, OH), 1.29 (d, ^3J = 5.7 Hz, 1H, OH). – ^{13}C NMR (75 MHz): δ = 144.5 (q), 142.4 (q), 142.2 (q), 141.5 (q), 135.9 (t), 130.4 (t), 129.9 (t), 129.2 (t), 128.6 (t), 128.5 (t), 128.3 (t), 126.9 (t), 124.3 (t), 123.4 (t), 115.6 (s), 80.7 (t, CHOH), 79.6 (t, CHOH), 57.2 (q, C-2), 55.2 (t, $CHPh_2$), 36.0 (s, CH_2). – MS: *m/z* (%) = 297 (1) [$M^{\cdot+}$ – (H_2O, C_3H_5)], 279 (1), 219 (3), 171 (15), 167 (100) [$CHPh_2^+$], 165 (16), 152 (10), 91 (10).

$C_{25}H_{24}O_2$ (356.5) Ber. C 84.24 H 6.79 Gef. C 83.81 H 6.99

4b,8b,12b,12d-Tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene [Tribenzotriquinacene (**1a**)]: A mixture of 10.5 g (33.0 mmol) of **4a**, 80 ml of chlorobenzene, and 5.0 ml of orthophosphoric acid (85%) is stirred vigorously and heated at 120°C (bath temp.) for 20 h. Upon cooling, long colorless needles grow from the solution, which are filtered off by suction and then washed with chlorobenzene, water, and ethanol to give **1a** (1.03 g, 11%). The product may be recrystallized from hot toluene or xylene; m.p. 390–391°C. – IR[42] (KBr): $\tilde{\nu}$ = 3069 cm^{-1}, 3021, 2976, 1480, 1453. – ^1H NMR[42] (300 MHz): 3 AA'BB' spin systems [δ_A = 7.38 (6H); δ_B = 7.12 (6H)], δ = 4.88 (d, ^3J = 9.7 Hz, 3H, 4b/8b/12b-H), 4.00 (d, ^3J = 9.7 Hz, 1H, 12d-H). – ^{13}C NMR (75 MHz): δ = 145.8 (q), 127.4 (t), 124.3 (t), 55.9 (t, C-4b/8b/12b), 51.2 (t, C-12d). – MS: *m/z* (%) = 280 (100) [$M^{\cdot+}$], 279 (41), 276 (14), 203 (18), 202 (17), 138 (10).

$C_{22}H_{16}$ (280.4) Ber. C 94.24 H 5.75 Gef. C 93.98 H 5.80

4b,8b,12b,12d-Tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno-[1,6-ab]indene [Methyltribenzotriquinacene (**1b**)]: To a solution of 165 g (500 mmol) of **4b** in 1.5 l of xylene is added 25 ml of orthophosphoric acid (85%), and the mixture is heated under reflux for 5–8 h while the water formed is removed through a water separator and the reaction mixture turns dark brown. The hot solution is then filtered through a pad of ca. 20 g of K_2CO_3, and the solution is concentrated by evaporation while the colorless product precipitates. Recrystallization from xylene or ethyl acetate gives **1b** (48.5 g, 33%) as large crystals; m.p. 244°C (xylene). – IR[42] (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3020, 2960, 2900, 1485, 1460, 755, 735. – ^1H NMR[6,42] (300 MHz): 3 AA'BB' spin systems [δ_A = 7.44 (6H); δ_B = 7.19 (6H)], δ = 4.47 (s, 3H, 4b/8b/12b-H), 1.68 (s, 3H, CH_3). – ^{13}C NMR[6] (75 MHz): δ = 145.6 (q), 127.6 (t), 124.5 (t), 63.7 (t, C-4b/8b/12b), 60.7 (q, C-12d), 27.6. – MS: *m/z* (%) = 294 (100) [$M^{\cdot+}$], 293 (9), 279 (40) [$M^{\cdot+}$ – CH_3], 278 (13), 277 (11), 276 (11), 217 (11), 215 (8), 178 (16), 138 (10).

$C_{23}H_{18}$ (294.4) Ber. C 93.84 H 6.16 Gef. C 93.73 H 6.27

12d-Ethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno-[1,6-ab]indene [Ethyltribenzotriquinacene (**1c**)]: To a solution of 69.0 g (200 mmol) of **4c** in 700 ml of xylene is added 10 ml of orthophosphoric acid (85%), and the mixture is heated under reflux for 10 h while the water formed is removed through a water separator. After cooling, the solution is washed with water, and the xylene is evaporated in vacuo. The viscous brown residue is distilled in a kugelrohr apparatus (200–210°C/0.03 mbar) to give a bright red, partially crystallizing oil. By addition of a few milliliters of benzene and then 100 ml of *n*-hexane, **1c** is converted into a colorless crystal powder. Recrystallization from ethanol affords half-inch long single crystals (16.7 g, 27%); m.p. 154°C. – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3025, 2958, 2932, 2869, 1474, 1453, 1380, 814. – ^1H NMR (300 MHz): 3 AA'BB' spin systems [δ_A = 7.44 (6H); δ_B = 7.17 (6H)], δ = 4.58 (s, 3H, 4b/8b/12b-H), 2.06 (q, 2H, CH_2), 1.02 (t, 3H, CH_3). – ^{13}C NMR (75 MHz): δ = 145.5 (q), 127.3 (t), 124.3 (t), 65.4 (q, C-12d), 60.6 (t, C-4b/8b/12b), 32.3 (s), 8.6. – MS: *m/z* (%) = 308 (98) [$M^{\cdot+}$], 279 (100) [$M^{\cdot+}$ – C_2H_5], 176 (19), 215 (14), 202 (8), 178 (25), 138 (13).

$C_{24}H_{20}$ (308.4) Ber. C 93.46 H 6.54 Gef. C 93.38 H 6.55

12d-Benzyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno-[1,6-ab]indene [Benzyltribenzotriquinacene (**1d**)]: To a solution of 20.3 g (50 mmol) of **4d** in 200 ml of xylene is added 5 ml of orthophosphoric acid (85%), and the mixture is heated under reflux for 5–8 h while the water formed is removed through a water separator and the reaction mixture turns dark yellow. The solution is then filtered through a pad of ca. 5 g of K_2CO_3, the solvent is evaporated, and the brown residue is redissolved in 20 ml of warm ethyl acetate. The product **1d** is precipitated by addition of ethanol as a colorless powder (3.33 g, 18%); m.p. 243°C. – IR[42] (KBr): $\tilde{\nu}$ = 3068 cm^{-1}, 3023, 2910, 1494, 1484, 1452, 1180, 1024, 756, 745, 703. – ^1H NMR[42] (300 MHz): 3 AA'BB' spin systems [δ_A = 7.39 (6H); δ_B = 7.14 (6H, partially overlapped)], δ = 7.14–7.28 (m, 5H, Ph), 4.79 (s, 3H, 4b/8b/12b-H), 3.31 (s, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 145.3 (q), 138.3 (q, Ph), 129.9 (t, Ph), 128.2 (t, Ph),

127.4 (t), 126.3 (t, Ph), 124.3 (t), 65.2 (q, C-12d), 61.3 (t, C-4b/8b/12b), 45.7 (s, CH_2). – MS: *m/z* (%) = 370 (31) [$M^{\bullet+}$], 292 (11), 279 (100, [$M^{\bullet+} - C_7H_7$], 278 (26), 276 (20), 178 (2), 91 (8).

$C_{29}H_{22}$ (370.5) Ber. C 94.01 H 5.99 Gef. C 93.84 H 5.73

12d-(Diphenylmethyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene [Benzhydryltribenzotriquinacene (**1e**)]: A suspension of 121 g (250 mmol) of **4e** in 1.2 l of toluene and 8 g of the ion exchange resin Amberlyst 15 (Fluka) is stirred magnetically and heated under reflux for 18 h while the water formed is removed through a water separator. The hot solution is filtered and then concentrated in a rotary evaporator under reduced pressure to precipitate a solid which is washed with toluene and then with ethanol to give **1e** as a colorless powder (31.3 g, 26%), m.p. 318–319°C. – IR[42] (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3030, 2950, 2930, 2860, 1600, 1480, 770, 755, 715, 705. – ^1H NMR[42] (300 MHz): 3 AA'BB' spin systems [δ_A = 7.37 (6H); δ_B = 7.14 (6H, overlapped)], δ = 7.30 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 4H), 7.08–7.17 (m, ca. 6H), 5.10 (s, 3H, 4b/8b/12b-H), 4.60 (s, 1H, $CHPh_2$). – ^{13}C NMR (75 MHz): δ = 145.3 (q), 142.4 (q, Ph), 129.3 (t, Ph), 128.2 (t, Ph), 127.4 (t), 126.3 (t, Ph), 124.0 (t), 68.7 (q, C-12d), 60.8 (t, C-4b/8b/12b), 59.7 (t, $CHPh_2$). – MS: *m/z* (%) = 446 (17) [$M^{\bullet+}$], 368 (13) [$M^{\bullet+} - C_6H_6$], 279 (100) [$M^{\bullet+} - CHPh_2$], 168 (30) [$CH_2Ph_2^+$], 167 (69) [$CHPh_2^+$], 165 (31), 152 (10).

$C_{35}H_{26}$ (446.6) Ber. C 94.13 H 5.87 Gef. C 93.44 H 5.63

12d-Allyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene [Allyltribenzotriquinacene (**1g**)]: To a solution of 3.56 g (10 mmol) of **4g** in 50 ml of chlorobenzene is added 3 ml of orthophosphoric acid (85%), and the mixture is stirred and heated to 130°C for 10 h. The usual workup (see below for reaction of **1f**) gives a black oil, from which the hydrocarbon mixture is separated by filtration of the solution in $CHCl_3$/*n*-hexane (1:1) through a pad of silica gel. Subsequent MPLC [CH_2Cl_2/*n*-heptane (1:3)] of this fraction yields **1g** as a light yellow oil (340 mg, 11%), which contains minor amounts (ca. 10%) of impurities and does not crystallize. Distillation in a kugelrohr apparatus (ca. 230°C/0.03 mbar) affords a light-yellow oil, a solution of which in *n*-pentane gives, upon cooling, colorless crystals; m.p. 150°C. – IR (neat): $\tilde{\nu}$ = 3068 cm^{-1}, 3026, 2927, 1599, 1493, 1476, 1453, 1025, 914, 740, 699. – ^1H NMR (300 MHz): 3 AA'BB' spin system [δ_A = 7.43 (6H); δ_B = 7.17 (6H)], δ = 5.75–5.91 (m, 1H, $CHCH_2$), 5.19 [dq, ^3J = 16.9 Hz, 1H, (*E*)-CHCH*H*), 5.07 [dd, ^3J = 10.2 Hz, 1H, (*Z*)-CHCH*H*), 4.63 (s, 3H, 4b/8b/12b-H), 2.74 (d, ^3J = 7.1 Hz, 2H, $CH_2CH=CH_2$). – ^{13}C NMR (75 MHz): δ = 145.2 (q), 134.0 (t, $CH=CH_2$), 127.4 (t), 124.2 (t), 118.4 (s, $CH=CH_2$), 64.0 (q, C-12d), 60.9 (t, C-4b/8b/12b), 44.3 (s, CH_2). – MS: *m/z* (%) = 320 (89) [$M^{\bullet+}$], 279 (38), 278 (100) [$M^{\bullet+} - C_3H_6$], 276 (19), 229 (23), 215 (14), 191 (12), 139 (8), 138 (10), 115 (5), 91 (8).

$C_{25}H_{20}$ (320.4) Ber. C 93.71 H 6.29 Gef. C 93.63 H 6.23

Attempted Cyclodehydration of **4f**. – *Synthesis of 2,3-Dihydro-2-phenyl-1H-inden-1-ol* (**14**): To a solution of 19.6 g (50.0 mmol) of **4f** in 150 ml of chlorobenzene is added 10 ml of orthophosphoric acid (85%), and the mixture is stirred and heated to 130°C for 24 h. After cooling, the solution is filtered through a pad of ca. 10 g of K_2CO_3, and the solvent is evaporated in vacuo to give a brownish, pasty residue, which contains ca. 60% of the indenol **14** (^1H NMR). The mixture is redissolved in 300 ml of warm chloroform and then precipitated by the addition of 100 ml of *n*-heptane to give the product **14** (4.16 g, 40%) as a colorless powder. This material is sublimed in a kugelrohr apparatus (ca. 170°C/0.03 mbar) to give the indenol **14** as a colorless solid, which is recrystallized from acetone to give colorless platelets; m.p. 152°C. – IR (KBr): $\tilde{\nu}$ = 3226 cm^{-1} (br.), 3063, 2929, 2859, 1606, 1493, 1455, 1445, 1060, 889, 759, 736, 687. – ^1H NMR (300 MHz): δ = 7.73 (d, ^3J = 7.1 Hz, 2H), 7.56 (d, ^3J = 7.2 Hz, 1H), 7.41 (t, ^3J = 7.2 Hz, 2H), 7.1–7.4 (m, 4H), 7.06 (s, 1H, ArCH=C), 5.54 (s, 1H, C*H*OH), 2.15 (s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 148.5 (q), 145.2 (q), 142.0 (q), 133.8 (q), 128.8 (t), 128.7 (t), 127.9 (t), 126.7 (t), 126.6 (t), 126.1 (t), 123.6 (t), 121.3 (t), 76.4 (t, CHOH). – MS: *m/z* (%) = 208 (100) [$M^{\bullet+}$], 179 (27), 178 (31), 165 (12), 152 (7), 130 (28), 102 (14).

$C_{15}C_{12}O$ (208.3) Ber. C 86.51 H 5.81 Gef. C 86.26 H 5.96

2,3-Dihydro-2-phenyl-1H-inden-1-one (**15**): All following procedures have to be carried out with exclusion of light. A suspension of 1.04 g (5.0 mmol) of **14** in 50 ml of diethyl ether is stirred with 20 g of activated manganese dioxide (Merck). The reaction is complete after 10 min (as monitored by TLC and MS). The mixture is filtered to give an orange-red solution, and the solvent is evaporated to give an orange, readily crystallising oil. Recrystallization from CH_2Cl_2/*n*-hexane yields **15** (0.97 g, 94%) as fine, orange crystals; m.p. 76°C (ref.[30] 75–76°C). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 3053, 3035, 1701, 1602, 1485, 1453, 1444, 1264, 906, 742, 692. – ^1H NMR (300 MHz): δ = 7.78 (d, ^3J = 6.8 Hz, 2H), 7.61 (s, 1H, ArCH=C), 7.29–7.46 (m, 5H), 7.19 (t, ^3J = 7.0 Hz, 1H), 7.11 (d, ^3J = 7.2 Hz, 1H). – ^{13}C NMR (75 MHz): δ = 196.0 (q, CO), 143.8 (q), 142.5 (t), 136.2 (q), 134.1 (t), 131.3 (q), 131.1 (q), 128.7 (t), 128.5 (t), 127.2 (t), 122.9 (t), 121.9 (t). – MS: *m/z* (%) = 206 (100) [$M^{\bullet+}$], 178 (24), 176 (16), 152 (9), 103 (5), 88 (7), 76 (12).

4b,9,9a,10-Tetrahydroindeno[1,2-a]indene (**13**): To a solution of 20.6 g (100 mmol) of **11**[26a] or 22.4 g (100 mmol) of 2-benzyl-1-indanol[26a] in 150 ml of chlorobenzene is added 10 g of polyphosphoric aicd, and the mixture is stirred and heated at 130°C for 40 h. After cooling, the solution is filtered through a pad of ca. 10 g of K_2CO_3, and the solvent is removed in vacuo. The brown, partially crystallized residue is distilled in a kugelrohr apparatus (b.p. 180°C/0.03 mbar) to give the crude product (18.0 g) as a bright-yellow, readily solidifying oil. Recrystallization from ethanol yields **11** (17.4 g, 85%) as long needles or plates; m.p. 96°C. The spectroscopic data are in accord with the literature data[28,29].

☆ Dedicated to Professor *Hans-Friedrich Grützmacher* on the occasion of his 60th birthday.

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[500/91]

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1a: 120022-86-8 / **1b**: 91158-95-1 / **1c**: 140389-04-4 / **1d**: 91158-96-2 / **1e**: 91158-97-3 / **1g**: 140389-05-5 / **2a**: 606-23-5 / **2b**: 876-83-5 / **2c**: 27606-61-7 / **2d**: 890-44-8 / **2e**: 1821-21-2 / **2h**: 134361-57-2 / **3b**: 91158-88-2 / **3c**: 140388-92-7 / **3d**: 91158-89-3 / **3e**: 63488-20-0 / **3f**: 63488-21-1 / **3g**: 140388-93-8 / **3i**: 140388-94-9 / **4a**: 140388-95-0 / **4b** (isomer 1): 140388-96-1 / **4b** (isomer 2): 140388-97-2 / **4c** (isomer 1): 140388-98-3 / **4c** (isomer 2): 140409-81-0 / **4d**: 140388-99-4 / **4e**: 140389-00-0 / **4e″**: 140389-01-1 / **4f**: 140409-82-1 / **4g** (isomer 1): 140389-02-2 / **4g** (isomer 2): 140389-03-3 / **11**: 93433-54-6 / **13**: 21013-44-5 / **14**: 140389-06-6 / **15**: 19096-31-2 / dimethyl phthalate: 131-11-3 / 2,6-dimethylheptanone: 108-83-8 / diphenylmethanol: 91-01-0 / allyl iodide: 556-56-9 / triphenylmethanol: 76-84-6 / 2-(diphenylmethyl)-2,3-dihydro-1*H*-inden-1-ol-3-one: 140389-07-7