Benzoanellated Centropolyquinanes, 14[1]

Synthesis of Tribenzotriquinacene by Stereocontrolled Cyclization of Phenyl-Substituted C_s-Diindans (4bα,9,9aα,10-Tetrahydroindeno[1,2-*a*]indenes)☆

Dietmar Kuck*, Ekkehard Neumann, and Andreas Schuster

Fakultät für Chemie, Universität Bielefeld,
Universitätsstraße 25, D-33615 Bielefeld

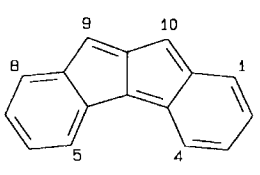
Received July 19, 1993

Key Words: Triquinacenes / Indenoindenes / *syn* Elimination, thermal / Conformational effects

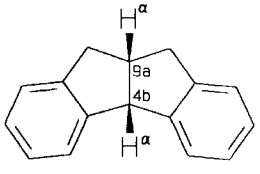
The synthesis of tribenzotriquinacene **4** by a stepwise cyclization strategy involving phenyl-substituted diindan intermediates is discussed in detail. Based on the determination of the *anti* (α) stereochemistry of the previously known phenyldiindanone **8** by standard electron impact mass spectrometry as well as on synthetical evidence (**8** → **12** → **14**), the conversion of **8** to the *syn* (β) phenyl-substituted isomer **20** by means of dehydrogenation-rehydrogenation sequences has been achieved. In particular, the preparation of the isomeric diindenones **15** and **16** as key synthetic intermediates by thermal *syn* elimination of the corresponding phenylsulfinyl and phenylseleninyl ketones **22** and **25** is described and contrasted to a bromination/dehydrobromination approach adopted from a previous report. The synthesis is completed by reduction of **20** to diindanol **27** followed by cyclodehydration, giving **4** in 14–19% overall yield from **8**. Non-cyclizing dehydration of **27** and the isomeric diindanol **9** gives the $\Delta^{4b,9}$-diindene **30** as the most stable non-cyclized isomer of **4**. The steric effect of the *syn*- or *anti*-oriented phenyl substituents on the preferred conformation of the diindan skeleton is deduced from the contrasting vicinal ^1H-^1H spin coupling observed for the stereoisomers, e.g. the 9-phenyldiindans **28** and **29**.

In 1957 Baker, McOmie et al.[2] reported on the synthesis of novel aromatic compounds bearing benzoanellated pentalenes as parent systems. Among these, 1,2:5,6-dibenzopentalene, now generally called indeno[1,2-*a*]indene (**1**), represented a particularly interesting target system because of its relatively low stability[3]. While the synthesis of the fully unsaturated "diindene" **1** has never been achieved to date[3b], the 4b,9,9a,10-tetrahydro derivative **2** was prepared by Baker et al.[2] and, in due course, by others performing independent approaches[4,5]. Baker et al.[2] also reported on the synthesis of several 9,10-substituted derivatives of type **3**, without, however, defining the stereochemistry of these compounds.

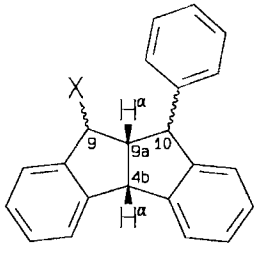
In the course of our studies on the synthesis and properties of centrically condensed, polycyclic indan hydrocarbons ("centropolyindans"[6]), the unsubstituted tribenzotriquinacene **4** represented a particularly challenging target. In contrast to the facile access to several derivatives bearing an alkyl substituent at C-10 (*centro*-alkylated tribenzotriquinacenes)[7], we have developed a very short (three-step) yet low-yield synthesis of **4** only recently[4] using a twofold cyclodehydration strategy of suitably substituted 2-benzhydryl-1,3-indandiols[8,9]. Therefore, it appeared interesting to pursue synthetic pathways to **4** starting from the phenyl-substituted diindan precursors (e.g. **3**) described by Baker et al.[2] In particular, we envisaged a *single* cyclodehydration for the construction of the third indan unit. To this end, the orientation of the phenyl substituent at C-10 had to be determined unambiguously and, as will be shown below, a method for epimerization of this stereogenic center had to be developed. The synthesis of **4** and the remarkably high reactivity of this triply benzoanellated triquinacene towards strong bases both in solution and in the gas phase have been communicated recently[10]; in the present paper, we report in detail on the synthesis and the stereochemistry of 10-phenyl-substituted "*fuso*"-diindans[6,11] of type **3** and on the stepwise preparation of **4**.



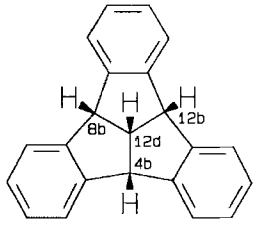
1



2



3



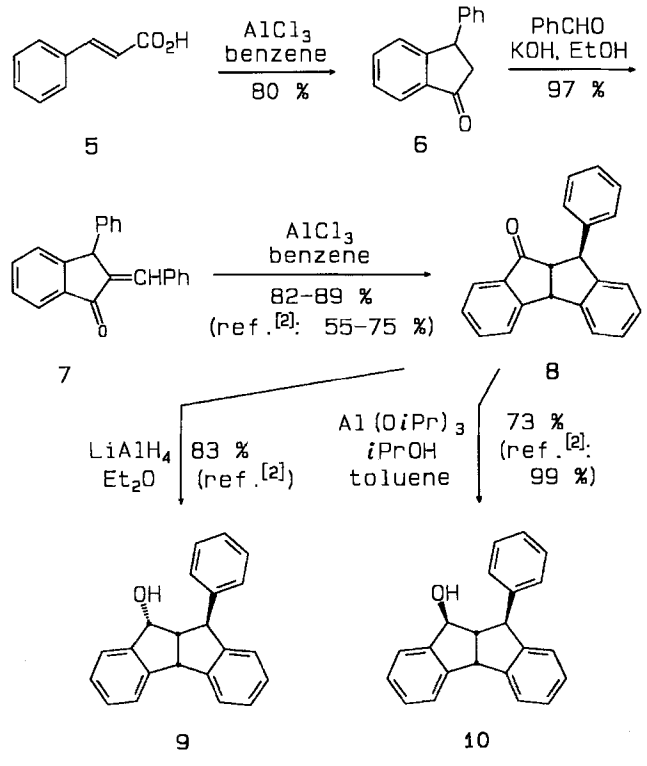
4

  0009–2940/94/0101–0151 $ 10.00+.25/0

Stereochemistry of Baker's Diindans

The 10-phenyldiindanone **8** represents the first important synthetic intermediate of this work. According to the previous report[2], **8** is prepared in three steps from cinnamic acid (**5**), benzene, and benzaldehyde (Scheme 1). We considerably improved this sequence, in particular by decreasing the amount of the catalyst used in the third step (see Experimental). Thus, the diindanone **8** is easily accessible now from **7**[12] on a 70-g scale in yields of 82–89%.

Scheme 1



As shown previously[2], reduction of **8** with $LiAlH_4$ or $Al(OiPr)_3$ leads, with high selectivity, to either of two stereoisomeric alcohols (previously termed "isomer A" and "isomer B", respectively)[2]. On the basis of spectroscopic and synthetic results, we identified these alcohols as the epimeric 9β-hydroxy-10α-phenyldiindan **9** and 9α-hydroxy-10α-phenyldiindan **10** and, as a consequence, the diindanone **8** as the 10α-phenyl stereoisomer. Finally, and not surprisingly, the *cis* (i.e. 4a*H*,9a*H*) fusion of the two five-membered rings in **8**–**10**, which had been already assumed by Baker et al.[2], is unambiguously corroborated by these stereochemical assignments.

The first hints to the stereochemistry of the two alcohols **9** and **10** were obtained from their standard electron impact (EI) mass spectra (Figure 1, Table 1). The stereoisomer **9** formed by reduction with $LiAlH_4$ exhibits, in contrast to **10**, a distinctively fast elimination of water from the molecular ion. This is a typical feature of stereoisomers bearing a hydroxy group oriented sterically favorably in the vicinity of a relatively weak C–H bond, such as those in the benzhydrylic C-10 position of **9** and **10**. Among the four possible diastereomers **9**, **10** (Scheme 1) and **26** and **27** (see below, Scheme 6) comprising the relatively rigid *cis*-bicyclo-[3.3.0]octane (i.e., the *fuso*-diquinane) skeleton, only one, namely **9**, has the entropically favorable mutual 1,3-*syn* orientation of the 9-OH group and the benzhydrylic "activated" C(10)–H bond. In the case of **10** as well as of **26** and **27**, loss of water should take place only by unfavorable *syn*-1,2 elimination or, more likely, after isomerization of the carbon skeleton, which, in general, cannot compete with regioselective 1,3- and 1,4-elimination of water[13–16].

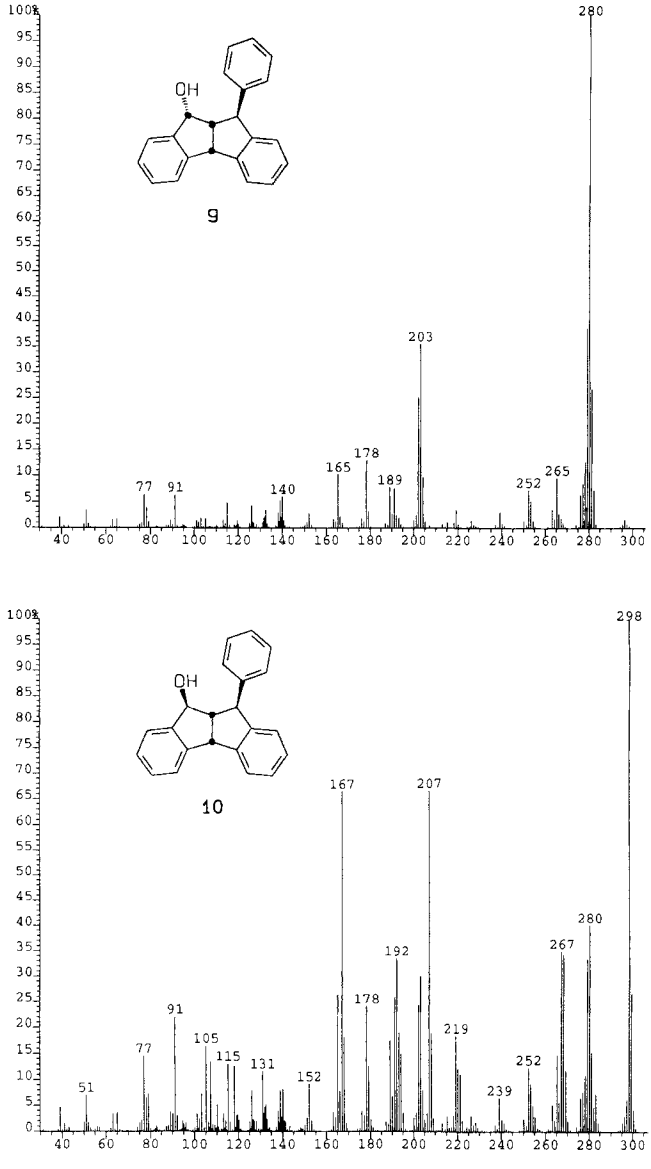


Figure 1. Mass spectra (EI, 70 eV) of the stereoisomeric diindanols **9** and **10**

The mass spectrometric assignment of the stereochemistry of **9** as 10α-phenyl isomer allows us, without any doubt, to deduce the same "*exo*" orientation for the phenyl group at C-10 of **10** and of the precursor ketone **8**. Of course, **8** has to be considered thermodynamically more stable than the stereoisomer **20** (Scheme 4) since the phenyl group is situated above the convex side of the diindan framework[17]. The stereochemistry of **8**–**10** is also corroborated by a

Table 1. Stereospecific loss of water in the EI mass spectra (70 eV) of the 10-phenyldiindan-9-ols **9**, **10**, **12**, and **27**[a]

Compound	$[M^{\bullet+}]$[b]	$[M^{\bullet+} - H_2O]$[b]	$[M^{\bullet+} - H_2O]/[M^{\bullet+}]$
9	<0.5	100	>200
10	100	39	0.4
27	57	100	1.8
12	29	55[c]	1.9

[a] Temperatures: source 170°C, direct inlet probe 180°C. – [b] In % B. – [c] Base peak at *m/z* 279, corresponding to $[M^{\bullet+} - (H_2O, C_7H_7)]$.

Table 2. Partial ^{1}H-NMR spectra of 10α- and 10β-phenyldiindans (300 MHz, $CDCl_3$)

	Chemical shifts (δ)						Coupling constants (^3J, Hz)		
	4bα[a]	9aα	9α	9β	10α[a]	10β[a]	4b,9a	9,9a	9a,10
8	5.11	3.54	–	–	–	4.78	7.1	–	3.0
20	4.97	3.91	–	–	4.94	–	7.3	–	11.7
9	4.73	3.59	5.43	–[b]	–	4.63	7.5	7.3	6.5
10	4.98	3.27	–[c]	5.21	–	4.15	7.2	2.2	6.5
27	4.61	3.85	5.24	–[c]	4.80	–	7.2	7.0	9.2
28	4.78	3.38	3.21	3.01	–	4.02	7.6	α 7.7 β 2.4	7.1
29	4.69	3.69	2.52[c]	2.59[c]	4.78	–	7.6	7.9 9.0	8.2

[a] Assignments of the benzhydrylic proton resonances by ^{1}H-^{1}H COSY spectrometry, using the ^4J coupling with the arene *ortho* protons. – [b] Hydroxyl proton resonances $\delta_{9\beta\text{-OH}} = 1.80$ (**9**); $\delta_{9\alpha\text{-OH}} = 1.75$ (**10**); $\delta_{9\beta\text{-OH}} = 1.3$ (**27**). – [c] Tentative assignments.

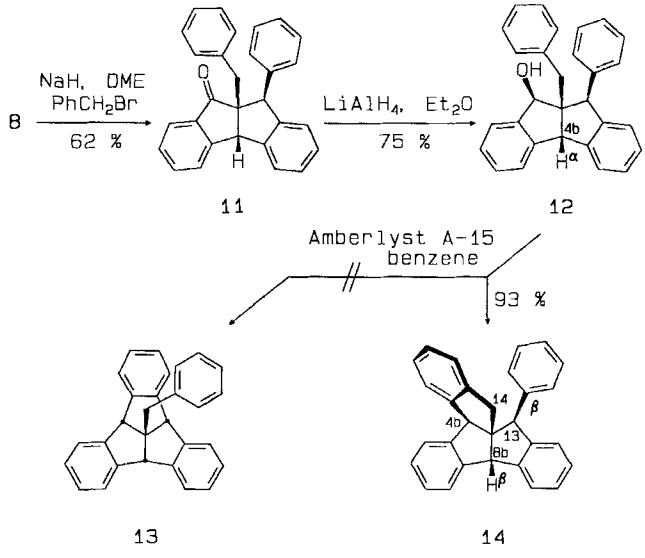
number of chemical transformations of **8**, as will be shown below.

Noteworthily, standard ^{1}H-NMR spectrometry of **8**–**10** (Table 2) does not allow an unambiguous stereochemical identification of the two alcohols, in spite of distinctly different coupling constants found for **9** and **10**. Whereas the small coupling constant of one of the benzydrylic protons of **8** in fact suggests the α orientation of the phenyl group ($^3J_{9a,10} = 3.0$ Hz), the two alcohols **9** and **10** do not exhibit a similar effect. Notably, the small coupling constant found for **10** ($^3J_{9,9a} = 2.2$ Hz) involves the carbinol proton (9-H), not the benzhydrylic one. Obviously, as observed in general for cyclopentane derivatives[18], the conformation and thus the vicinal ^{1}H-^{1}H coupling of the diquinane moiety of **8**–**10** is strongly affected by the substituents (Figure 1)[19,20]. For comparison, Table 2 comprises also the partial ^{1}H-NMR spectra of the 10β-phenyl ketone **20**, the corresponding alcohol **27** as well as those of the two stereoisomeric 10-phenyldiindans **28** and **29**. As will be shown below, all of the new 10β-phenyl ("*syn*") isomers **20**, **27**, and **29** in fact exhibit relatively large vicinal ^{1}H-^{1}H coupling constants, as expected.

Baker et al. also reported on various attempts to dehydrate the alcohols **9** and **10** in order to introduce additional double bonds into the diindan framework (cf. **1**). It is remarkable that these authors already considered, as an "interesting possibility"[2], the formation of tribenzotriquinacene **4** as a product of dehydration of these alcohols. On the basis of infrared spectrometry (viz. the *absence* of out-of-plane resonances indicative of *ortho*-phenylene groups) of the dehydration products isolated in very low yields, the formation of **4** was excluded[2]. It is evident that, without the potential of modern organic mass spectrometry and NMR spectroscopy, it was impossible to draw stereochemical conclusions simply from the non-occurrence of **4** upon dehydration of **9** and **10**. On the basis of the mass spectrometrical data presented here, however, it is clear that the α ("*anti*") orientation of the phenyl group at C-10 is the reason for the lack of cyclization.

The stereochemical assignment of epimeric alcohols **9** and **10** corresponds to the expected kinetic (or thermodynamic) control operating during the reduction of **8** with $LiAlH_4$ [or $Al(OiPr)_3$]. The steric shielding at the concave (β) side of the diindan skeleton of **8** leads to the attack of the AlH_4^- ion from the convex (α) side, in spite of the presence of the 10α-phenyl group. Under equilibrium conditions, however, the hydride transfer occurs also from the concave side of the diindan skeleton of **8**, generating the thermodynamically favorable 9α-alcohol **10**.

Scheme 2



A further proof for the orientation of the 10α-phenyl group in **8** was obtained from the course of the cyclodehydration of the 9aα-benzyl derivative of **10**, viz. **12**. This diindanol is synthesized in good yields from **8** by benzylation to give **11**, followed by reduction with $LiAlH_4$ (Scheme 2). Treatment of **12** with the ion-exchange resin Amberlyst A15 in benzene at reflux temperature gives the cyclodehydrated product, *difuso*-triindan **14**, in 93% isolated yield. The formation of 10-benzyltribenzotriquinacene **13** from **12** does not occur, again in accordance with the α preorientation of the phenyl group at C-10. In contrast, as has been shown recently[1b], the corresponding 10β-phenyl stereoisomer of **12** does undergo cyclodehydration to **13** with high selectivity (whereas the corresponding 10α-phenyl isomer of **14** is not formed). Thus, the course of the cyclization **12** → **14** corroborates, in line with the mass spectrometric data of the

simpler alcohols, the α orientation of the 10-phenyl group in **12** and hence in **8**–**11**.

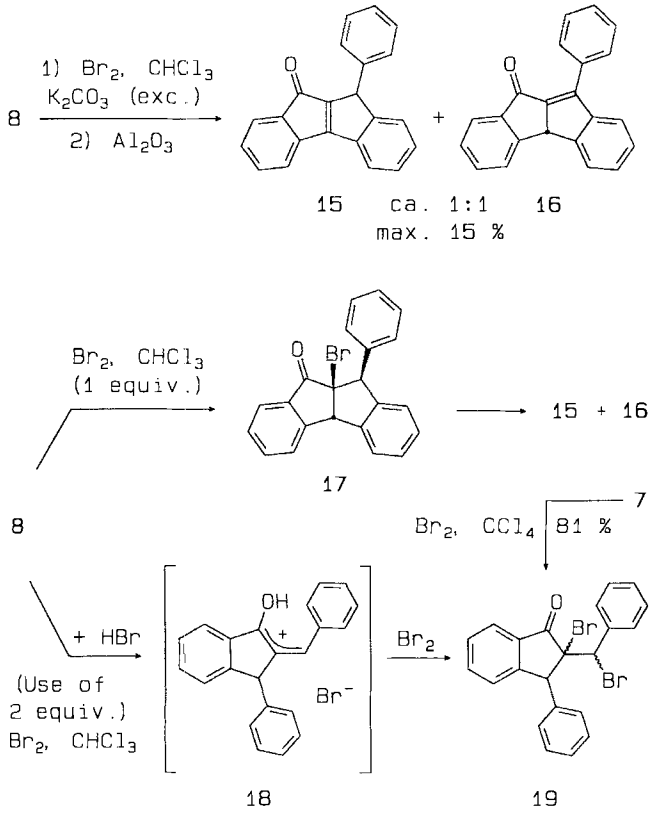
According to two-dimensional ^{1}H-NMR (NOESY and COSY) experiments, the hydroxy group in **12** is oriented to the convex (α) side of the diindan skeleton. A strong NOE is observed for the carbinol proton signal ($\delta_{9\beta\text{-H}} = 5.17$) and that of the benzhydrylic proton oriented to the concave side of the diindan skeleton ($\delta_{10\beta\text{-H}} = 4.48$). Moreover, the mass spectrum of **12** exhibits only a moderate loss of water from the molecular ions (55% B, Table 1), in line with the behavior of the non-benzylated diindanol **10**. These results suggest that, in contrast to the reduction of **8**, the presence of the 9aα-benzyl substituent adjacent to the 10α-phenyl group suppresses the attack of the AlH_4^- ion from the α side.

With the stereochemical results in hand, we pursued, on the basis of the previously reported ketone **8**[2], the epimerization of the benzhydrylic center at C-10 to generate phenyldiindan derivatives that may eventually undergo cyclization to tribenzotriquinacene **4**.

Epimerization of Baker's Diindan Ketone 8

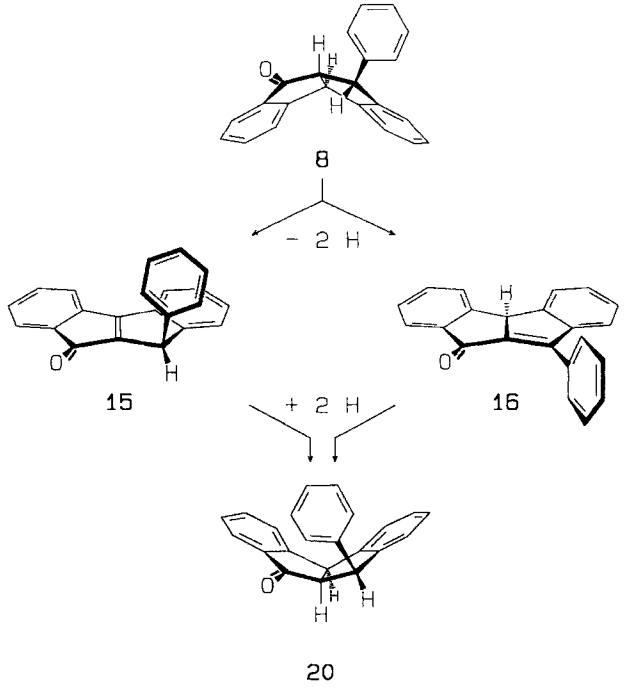
In the course of their attempts to introduce additional double bonds into the diindan framework of **2**, Baker et al.[2] generated, by bromination/dehydrobromination of **8**, an α,β-unsaturated ketone to which they assigned the structure of **15** (Scheme 3). The yields of the enone thus produced were rather low and not stated explicitly[21]. Nevertheless, for our purpose, the enone **15** promised to be a suitable substrate for the (apparent) inversion of the stereochemistry at C-10 of **8**.

Scheme 3



We expected that the strained double bond of **15** should selectively undergo catalytic rehydrogenation from the less hindered side because of the stereodifferentiating phenyl substituent at C-10. Thus, provided that the catalyst would not cause competing epimerization at C-10, inversion of the two centers of the diindan junction (C-4b–C-10) would give rise to an *indirect* flip of the phenyl group leading to the β ("*endo*") orientation (Scheme 4). Reduction of the resulting 10β-phenyl ketone **20** to a corresponding alcohol followed by acid-catalyzed cyclodehydration should then furnish the title compound **4**. In fact, as will be shown below, this route proved to be successful. As an interesting facet, it has been found that the enone **16** is formed along with the originally inferred isomer **15**. Fortunately, albeit not surprisingly, **16** undergoes the designed rehydrogenation to **20** as well (Scheme 4).

Scheme 4



Many attempts to reproduce the bromination/dehydrobromination, with at least moderate yields, on the originally reported or on enlarged scale were unsatisfactory. In every case the yields of the dehydro product were very low (<10%). The mixture of compounds (with the starting ketone **8** as the major component) obtained after the first step contained minor amounts of a product to which we tentatively attribute the structure **17** (Scheme 3). Interestingly, however, subsequent elution of this mixture through alumina, as described earlier[2], furnishes a mixture of *two* yellow compounds, as evident from thin layer chromatography, in an approximately 1:1 ratio. It is obvious on the basis of closely similar physical and chemical properties that the two yellow products have the structure **15** and **16**. Extensive modification of the reaction conditions[22] did not increase the combined yield of **15** and **16** beyond 15% (see Experimental), but the mixture of the isomeric α,β-unsaturated

ketones was produced irrespective of the method and conditions used.

Interestingly, use of an excess of bromine gives rise to the formation of the ring-opened dibromo ketone **19** in ca. 30% yield (Scheme 3), which has been fully identified by mass and NMR spectrometry as well as, pinpointedly, by preparative addition of bromine to the enone **7**. The formation of **19** suggests that at least a fraction of **8** undergoes a protolytic C–C bond cleavage at the "non-bridgehead", benzhydrylic ring position generating the highly stabilized oxyallyl ion **18**. Deprotonation of **18** to **7** followed by addition of bromine then gives **19**. Hence, part of the drawbacks of Baker's bromination/dehydrobromination sequence may be traced to the lability of **8** against hydrobromic acid formed during the first step. Accordingly, in our hands, the highest yield (15%) of **15/16** is obtained by working with bromine/chloroform solutions (instead of highly diluted bromine vapors[2]) but in the presence of an excess of potassium carbonate.

Another unfavorable feature of the bromination/dehydrobromination approach is the extremely low solubility of the enones **15** and **16** in most organic solvents. Therefore, significantly enlarged runs are excluded, in particular in the dehydrobromination step. Due to the extremely low solubility, full characterization of **15** and **16** by NMR spectrometry has not been accomplished up to now. Chromatographic separation of **15** and **16** is hampered by the finding that these enones readily interconvert on silica gel. At present, only fractions enriched with **15** or **16** have been obtained by repeated digestion of the crude product mixture and recrystallization. Finally, dimers of **15/16** have been observed by field desorption mass spectrometry (FD-MS) in varying amounts as byproducts[23]. The identity of the two isomers of the mixture of **15** and **16**, however, is confirmed by IR, ^{1}H- and ^{13}C-NMR-spectrometry, combustion analysis and by EI mass spectrometry. Besides the base peak for the molecular ion with *m/z* 294, the 70-eV standard mass spectrum exhibits a rather abundant $[M - H]^+$ ion (*m/z* 293, 65%) characteristic of styryl ketones[24] (viz. **16**) as well as an $[M - (H, CO)]^+$ peak (*m/z* 265, 42%). As will be shown below, a further proof for the identity of **15/16** is provided by the hydrogenation of the enone mixture[25].

Because of the low efficiency of the bromination/dehydrobromination approach, completely independent methods for the conversion of **8** to **15** and **16** have been elaborated. Attempts to dehydrogenate **8** with palladium chloride in *tert*-butyl alcohol[26] failed. In contrast, the thermal *syn* elimination method to generate α,β-unsaturated ketones[27,28] via the corresponding 9a-phenylsulfinyl or 9a-phenylseleninyl derivatives of **8** proved to be successful. Both of these three-step sequences have been carried out on a large preparative scale.

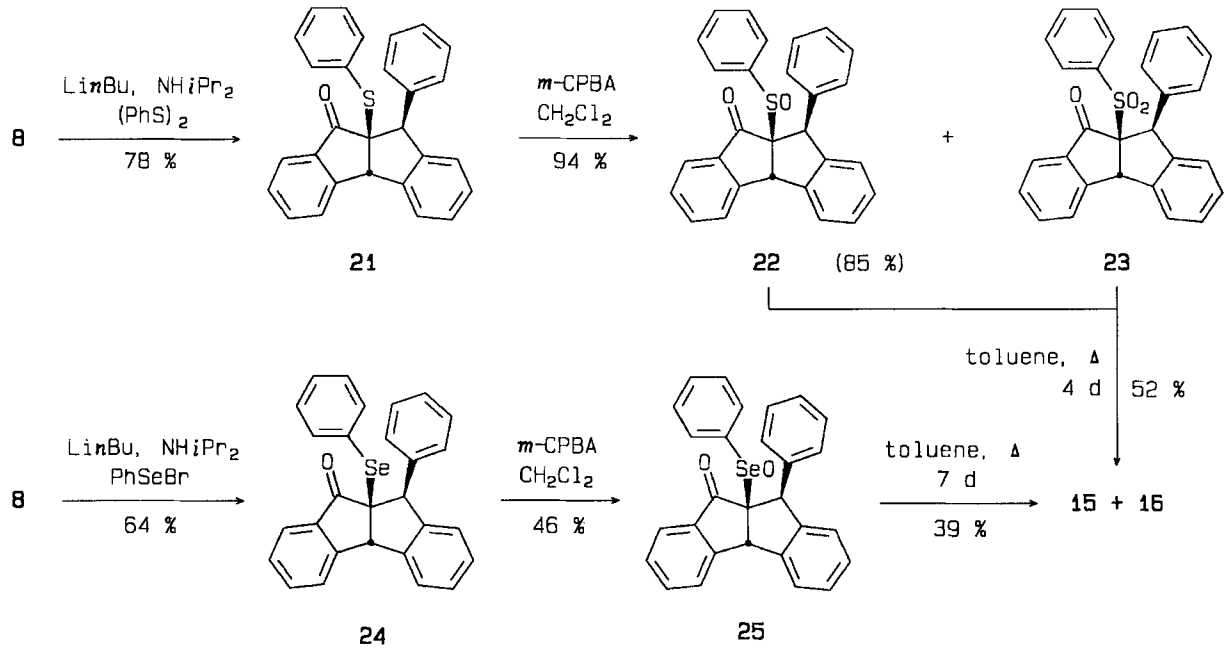
As shown in Scheme 5, treatment of **8** with diisopropylamide/diphenyl disulfide or benzeneselenyl bromide leads to the bridgehead-substituted derivatives **21** and **24**, respectively, in good yields[29]. Subsequent oxidation with *meta*-chloroperbenzoic acid (MCPBA) yields the corresponding sulfoxide **22** or selenium oxide **25**. MCPBA oxidation on a large scale produces varying amounts of the sulfone **23** as a byproduct. The thermal decomposition of **22** (or mixtures of **22** and **23**) as well as of **25** in toluene at reflux temperature furnishes a mixture of products which contains considerable amounts of the isomeric enones **15** and **16**. The crude product mixture is precipitated from the reaction mixture with petroleum ether. Repeated extraction of virtually dimeric byproducts with hot benzene gives a fine, yellowish powder which, according to TLC analysis, contains essentially **15** and **16**. The product thus obtained shows chemical and physical properties identical with those of the enone mixture produced by the bromination/dehydrobromination technique.

In summary, the sequence **8** → **21** → **22** → (**15/16**) turned out to be successful yet cumbersome. The purification of the enones obtained in this way is critical to sulfur-containing impurities that may hamper subsequent rehydrogenation. Nevertheless, in contrast to the bromination/dehydrobromination sequence, the sulfenylation route allows the synthesis of the mixture of **15** and **16** on a multigram scale. The alternative sequence via the phenylseleno compounds **24** and **25** does not offer decisive advantages.

Due to the extremely low solubility of **15** and **16**, the catalytic hydrogenation of the enones at atmospheric pressure and room temperature has to be carried out in dioxane (Scheme 6). With both of the isomers, it takes place with high stereoselectivity from the less sterically hindered side of the diindan framework giving the 10β-("*syn*"-)phenyldiindanone **20**. According to a ^{1}H-NMR analysis of the crude reaction mixture, the 10α-phenyl isomer **8** is not formed at all during the hydrogenation process. Slightly prolongated hydrogenation leads to complete reduction of the keto function giving the phenyldiindan **29** (see below). The purification of the *syn* ketone **20** is also critical in that this product tends to form solvent-containing gels. The crude product is obtained from methanol solutions in 83% yield and with ca. 85% purity. Further purification by flash chromatography and twofold recrystallization from *n*-hexane/chloroform yields **20** as analytically pure, colorless needles of m.p. 81°C. As a characteristic feature of **20**, the vicinal ^{1}H-^{1}H coupling is particularly large ($^3J_{9a\alpha,10\alpha}$ = 11.7 Hz, Table 2).

Reduction of **20** with $LiAlH_4$ in ether furnishes the corresponding alcohol **27** as a single stereoisomer (Scheme 6). The coupling constants in the ^{1}H-NMR spectrum of this product (Table 2) suggest the presence of a 9β-hydroxy group, as has been found for the alcohol **9** obtained from the epimeric 10α-phenyl ketone **8**. This observation is not surprising with regard to the additional steric shielding of the concave side of the diindan framework by the 10β-phenyl substituent of **20**, thus disfavoring the attack of the AlH_4^- ion to a much greater extent than in the case of **8**. Certainly, the 10β-phenyl diindanol **27** represents the thermodynamically least stable of the four possible diastereomeric alcohols. Therefore, we tried to synthesize the forth, 9α,10β diastereomer **26** (Scheme 6) by treatment of **20** with $Al(OiPr)_3$ (cf. **10**, Scheme 1). Unfortunately, and much to our surprise, **26** did not form at all. Obviously, hydride

Scheme 5



transfer to the concave (β) side is completely suppressed under these conditions[30].

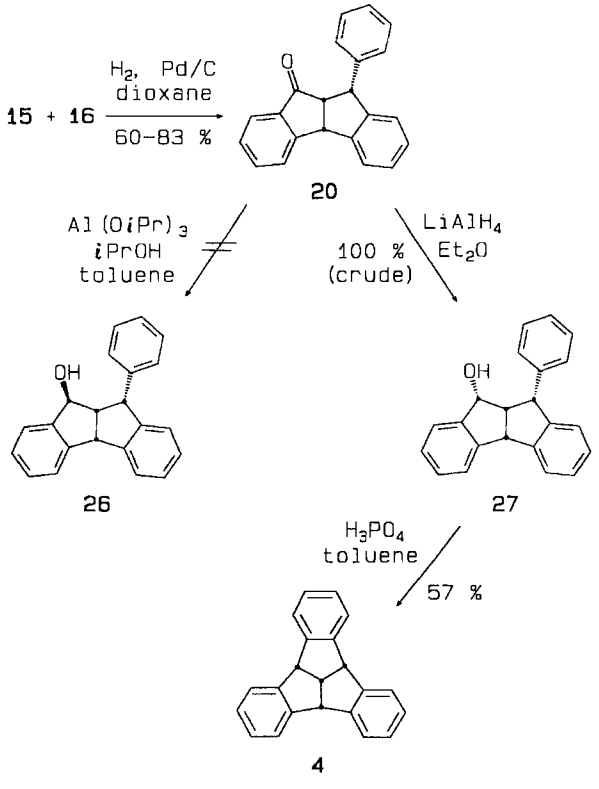
Characteristic ^{1}H-NMR signals of the diindanone **20** and the alcohol **27** are contrasted to those of the corresponding stereoisomers **8** and, respectively, **9** and **10**, in Table 2. In accordance with the stereochemistry assigned, all of the three ^3J coupling constants of the diquinane core of **20** and **27** are relatively large (≥ 7 Hz). The mass spectrometric fragmentation of **27** (Table 1) is also in line with the stereochemistry. In spite of the lack of a favorably oriented "activated" C–H bond, water loss from the molecular ions **27**$^{\bullet+}$ gives rise to the base peak in the standard EI spectrum, but the molecular ion peak is still remarkably intense (57% B), reflecting the intramolecular rearrangement prior to the water loss.

Tribenzotriquinacene and Related Hydrocarbons

According to the inverted configuration at C-10, acid-catalyzed dehydration of **27** in benzene or toluene at reflux temperature gives the cyclized product, tribenzotriquinacene **4**, in 55–60% yield (Scheme 6). The solubility of this hydrocarbon in organic solvents is extremely low; it readily crystallizes from the hot reaction mixture and is completely precipitated after cooling to room temperature. The chemical and physical properties of **4** are identical with those of the product obtained by twofold cyclodehydration of 2-benzhydryl-1,3-indandiol[4]. Indeed, the IR spectrum of **4** exhibits the out-of-plane bands (appearing as a narrow doublet at $\tilde{\nu}$ = 742 and 750 cm^{-1}) characteristic of the three *ortho*-phenylene groups[31,32], which led Baker et al.[2] to exclude, correctly, the formation of **4** during their dehydration experiments.

Finally, some congeners of **4** are described (Scheme 7) which represent the parent hydrocarbons of the 10α- and

Scheme 6



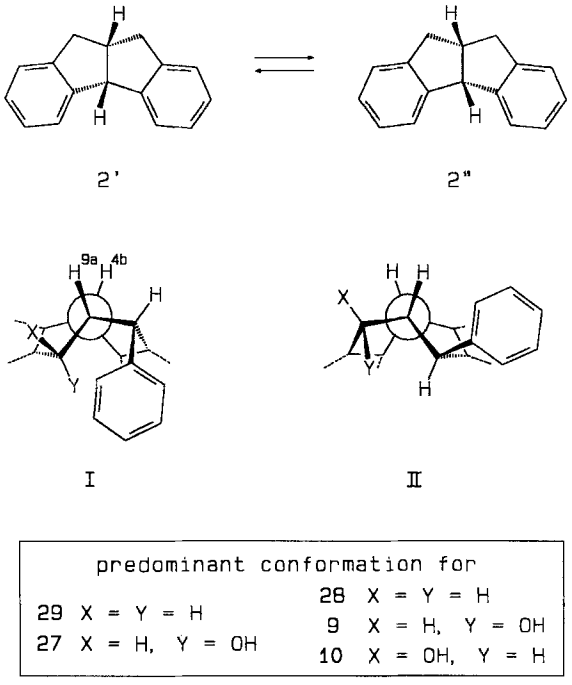
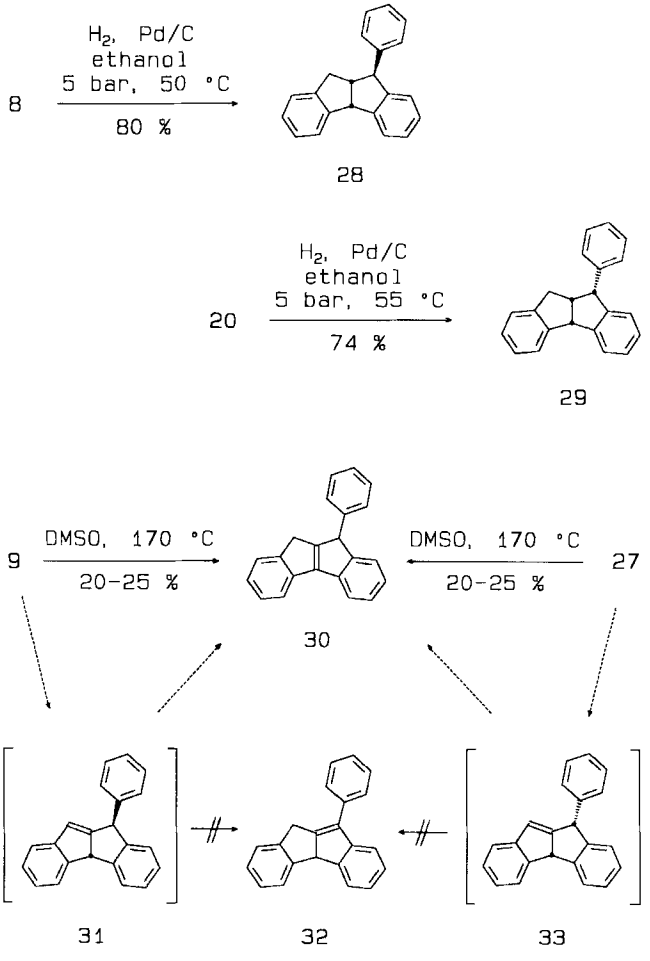


Figure 2. Conformational equilibrium of the diindan framework and predominant conformation of *syn*- and of *anti*-phenyl substituted diindans

10β-phenyl-substituted diindans of type **3**. As mentioned above, the 10β-phenyldiindan **29** is easily formed by catalytic hydrogenolysis of **20**. Under medium-pressure conditions (3–4 bar at room temp.), the reduction is completed within two hours without detectable epimerization at C-10. The corresponding stereoisomer **28** is prepared under the same conditions from the 10α-phenyldiindanone **8** and is identical with the hydrocarbon synthesized previously[2] by Wolff-Kishner reduction. The two readily crystallizing diindans exhibit characteristic ^{1}H-^{1}H coupling constants (Table 2). Again in line with its stereochemistry, the spectrum of the 10β-phenyl isomer **29** exhibits only large vicinal spin coupling ($^3J \geq 7.6$ Hz). Interestingly, the 10α isomer **28** again shows both a large and a small vicinal ^{1}H-^{1}H coupling, viz. $^3J_{9a\alpha,10b} = 7.1$ and $^3J_{9\beta,9a\alpha} = 2.4$ Hz. A similar feature is found for the 9α-diindanol **10** ($^3J_{9\beta,9a\alpha} = 2.2$ Hz).

The pronounced differences of the ^3J values may be understood by considering the directive influence of the bulky phenyl substituent at the diindan framework. Whereas in the parent system the two rotamers **2'** and **2"** (Figure 2) are equivalent, the β-phenyl-substituted derivatives adopt predominantly the conformation shown in **I**, hence minimizing the steric repulsion at the concave side of the diindan framework. Notably, all of the diquinane dihedral angles ∢(H–C–C–H) in form **I** are in the range of 0–30 or 150–180°. In contrast, the isomers bearing an α-phenyl substituent preferentially exist as rotamers **II**, thus minimizing the (weak) interaction of the phenyl group with the hydrogen atoms at the convex side of the molecules. As a characteristic feature of form **II**, one of the dihedral angles (drawn in bold in Figure 2) is near 90°, as reflected by the small ^3J value in **28** and **10**. The β-phenyldiindanone **20** is likely to adopt a conformation similar to **I** as well, whereas that of the α-phenyl isomer **8** should approach form **II**. Of course, the flattening of the diindan skeleton due to the carbonyl sp^2 center gives rise to a decreased dihedral angle H–C–C–H at C-9–C-10, in line with the particularly small $^3J_{9a-10}$ value found for **8**. Thus finally, the features of the ^{1}H-NMR spectra of Baker's diindan derivatives – which their stereochemical ambiguities at the outset of our work – may be rationally traced to the distinctive conformational behavior of the diindan skeleton[17,20].

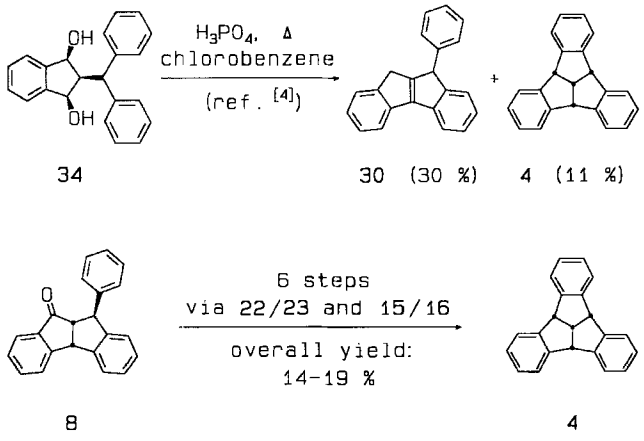
Scheme 7



In the course of our unsuccessful attempts to prepare the elusive diastereomer **26**, we studied the dehydration of the isomers **9** and **27** in dimethyl sulfoxide[33], hoping to stereospecifically produce the isomeric olefins **31** and **33**, respectively. Indeed, no cyclization occurs under these dehydration conditions as expected on the basis of previous findings[34]. However, instead of **31** and **33** a single diindene (m.p. 185°C) is obtained in low yield, to which we ascribe the structure **30** on the basis of ^{1}H-^{1}H COSY measurements (see Experimental). Baker et al.[2] already obtained, besides other dehydration products, a non-cyclized "anhydro" product with m.p. 179–180°C from both **9** and **10** in very low yield. The olefin **30** formed in the present study is probably identical with that reported by Baker. Curiously en-

ough, **30** – not **32**, as postulated in our previous paper[4,35] – is formed as the major side product of the synthesis of tribenzotriquinacene **4** by cyclodehydration of 2-benzhydryl-1,3-indandiol **34** (Scheme 8)[4]. As a bis-endocyclic, tetrasubstituted alkene, **30** should be the most stable isomer among **30**–**33**, in line with the high stability of the related 1,2,3,4,5,6-hexahydropentalene[36,37]. Obviously, extremely mild dehydration conditions would be necessary to prevent the shift of the double bond in the hypothetical diindenes **31** and **33**.

Scheme 8



In conclusion, a multistep synthesis of tribenzotriquinacene **4** based on readily available phenyl-substituted diindan precursors has been developed. Key step of the overall sequence is the (indirect) epimerization at C-10, bearing the phenyl group, to eventually achieve acid-catalyzed cyclodehydration of the formerly elusive "*endo*" diindan alcohol **27** to give **4**. Although this route to **4** is notably more cumbersome than the route employing twofold cyclodehydration of 2-benzhydryl-1,3-indandiol **34**[4], it offers an interesting and alternative synthetic access to more highly fused centropolyindans and their derivatives. The stereochemical and conformational analyses accompanying the synthetic efforts presented here shed some additional light on the peculiarities of 9,10-substituted 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indenes (C_s-centrodiindans).

Financial support of this work by the *Deutsche Forschungsgemeinschaft* (DFG Ku 661/1–2) is gratefully acknowledged.

Experimental

Melting points (uncorrected): Büchi 512 and Electrothermal melting point apparatus. – IR: Perkin-Elmer 377. – UV: Beckman model 25. – ^{1}H NMR: Bruker AM 300, Bruker WP 80; $CDCl_3$/TMS. – ^{13}C NMR: Bruker AM 300 (*J*-modulated spin-echo experiment); $CDCl_3$/TMS, if not stated otherwise. COSY and NOESY measurements Bruker AM 300 and Bruker AC 250 P. – MS: Finnigan MAT 311 A, Finnigan MAT CH 5 DF, and VG Analytical Autospec (Figure 1); EI, 70 eV. – Combustion analyses: Perkin-Elmer 240 and LECO CHNS-932 Analysator. – MPLC: Kieselgel 60 (LiChroprep 30–65 µm, Merck) with Besta E 100 and Besta UV 1. – TLC: Kieselgel 60 (F 254) on Al foil (Merck).

(4ba,9aa)-9a,10-Dihydro-10a-phenylindeno[1,2-a]inden-9(4bH)-one (**8**) is synthesized by a three-step sequence starting from **5** (Scheme 1). It has been considerably improved in the third step, in particular, as compared to the receipt given in the literature[2]. 3-Phenyl-1-indanone (**6**) is allowed to react with benzaldehyde on a half-mol scale to give 2-benzylidene-3-phenyl-1-indanone (**7**) in 97% yield. The crude **7** is dried in vacuo at 80°C and then recrystallized from ethanol/ethyl acetate (ca. 10:1); m.p. 156–157°C (158°C[12]). – To a mechanically stirred solution of **7** (50.0 g, 169 mmol) in 1.2 l of dry benzene is added aluminium chloride (115 g, a fivefold molar excess only!) in small portions. The mixture is heated to reflux for 12 h, then allowed to cool to room temp., and then poured into ice water. The resulting suspension is extracted several times with benzene (if this solvent is to be recycled in subsequent runs), and the combined extracts are washed with aqueous $NaHCO_3$ and dried with $MgSO_4$. Evaporation of the solvent gives an oily, orange residue, which is redissolved in methanol/ethyl acetate (ca. 9:1). The solution is heated to reflux with ca. 10 g of charcoal for 20 min, filtered through a thin pad of silica gel and then allowed to cool to 4°C to give **8** as bright-yellow crystals (41.0–44.5 g, 82–89%); m.p. 132–134°C (132°C[2]). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 1705, 1690, 1610, 1600, 1585, 775, 760, 755, 745, 700, 685. – ^{1}H NMR (300 MHz): δ = 7.79 (d, ^3J = 7.6 Hz, 1H), 7.74 (d, ^3J = 7.7 Hz, 1H), 7.65 (td, ^3J = 7.5, ^4J = 1.1 Hz, 1H), 7.52 (d, ^3J = 7.6 Hz, 1H), 7.39 (t, ^3J = 7.4 Hz, 1H), 7.15–7.35 (m, 7H), 7.03 (d, ^3J = 7.5 Hz, 1H), 5.11 (d, $^3J_{4b,9a}$ = 7.1 Hz, 1H, 4b-H), 4.78 (d, $^3J_{10,9a}$ = 3.0 Hz, 1H, 10-H), 3.54 (dd, $^3J_{9a,4b}$ = 7.1, $^3J_{9a,10}$ = 3.1 Hz, 1H, 9a-H). – ^{13}C NMR (75 MHz): δ = 207.0 (s, C=O), 156.4 (s), 145.7 (s), 144.6 (s), 143.0 (s), 135.7 (s), 135.4 (d), 128.8 (d), 128.1 (d), 128.0 (d), 127.7 (d), 126.6 (d), 126.3 (d), 125.7 (d), 124.5 (d), 61.5 (d), 52.7 (d), 50.2 (d). – MS, *m/z* (%): 296 (100) [M$^{\bullet+}$], 295 (23), 279 (16), 278 (15), 268 (12), 267 (18), 265 (22), 263 (9), 252 (18), 239 (10), 219 (20), 218 (36), 194 (14), 191 (24), 189 (45), 165 (31).

(4ba,9aa)-4b,9,9a,10-Tetrahydro-10a-phenylindeno[1,2-a]inden-9β-ol (**9**, Baker's isomer A) is prepared as described by Baker et al.[2] by reduction of **8** with $LiAlH_4$. It is obtained as colorless needles, m.p. 178°C (176–178°C[2]). – IR (KBr): $\tilde{\nu}$ = 3415 and 3365 cm^{-1} (s, br, OH), 3069, 3034, 2948, 2874, 1600, 1493, 1478, 1459, 1428, 1077 (s), 1072 (s), 1045 (s), 758, 744, 701, 631, 617, 606. – ^{1}H NMR (300 MHz): δ = 7.52 (d, ^3J = 7.5 Hz, 1H), 7.45 (quasi-t, $^3J \approx$ 4.5 Hz, 1H), 7.40 (quasi-t, $^3J \approx$ 4.4 Hz, 1H), 7.2–7.35 (m, 8H), 7.12 (t, ^3J = 7.5 Hz, 1H), 6.85 (d, ^3J = 7.4 Hz, 1H), 5.43 (d, ^3J = 7.3 Hz, 1H, C*H*OH), 4.73 (d, ^3J = 7.5 Hz, 1H, $CHAr_2$), 4.63 (d, ^3J = 6.5 Hz, 1H, $CHAr_2$), 3.59 (q, $^3J \approx$ 7.3 Hz, 1H, 9a-H), 1.8 (br s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 147.1 (s), 145.9 (s), 144.8 (s), 143.7 (s), 142.1 (s), 128.7 (d), 128.6 (d), 127.5 (d), 127.4 (d), 127.1 (d), 126.3 (d), 125.4 (d), 124.8 (d), 124.6 (d), 123.6 (d), 76.1 (d, CHOH), 59.2 (d), 53.6 (d), 50.3 (d). – MS, *m/z* (%): 280 (100) [M$^{\bullet+}$ – H_2O], 279 (39), 278 (13), 277 (8), 276 (6), 265 (10), 253 (5), 252 (7), 203 (36), 202 (25), 191 (8), 189 (8), 178 (13), 165 (10), 115 (5), 91 (6).

(4ba,9aa)-4b,9,9a,10-Tetrahydro-10a-phenylindeno[1,2-a]inden-9a-ol (**10**, Baker's isomer B)[2]: To a solution of Al(O*i*Pr)$_3$ (2.3 g) in 15 ml of 2-propanol is slowly added a solution of **8** (2.00 g, 6.8 mmol) in 25 ml of dry toluene. Gentle heating leads to a slow distillation of an acetone/toluene mixture over a total of 8 h while further toluene is added and the reaction is controlled by TLC. Addition of dilute sulfuric acid and ether and usual workup[2] afford the crude product, which is recrystallized from petroleum ether/THF to give **10** (1.47 g, 73%) as colorless crystals; m.p. 140–141°C (148°C[2]). – IR (KBr): $\tilde{\nu}$ = 3256 cm^{-1} (s, very br, OH), 3068, 3026, 2940, 2924, 2887, 1598, 1494, 1473, 1453, 1023 (s, C–O), 997, 753, 733, 721, 699, 641, 611. – ^{1}H NMR (300 MHz): δ = 7.52 (d, ^3J = 7.5 Hz, 1H), 7.44 (d, ^3J = 6.8 Hz, 2H),

7.2–7.37 (m, 8H), 7.15 (t, ^3J = 7.4 Hz, 1H), 6.90 (d, ^3J = 7.5 Hz, 1H), 5.21 (d, ^3J = 2.2 Hz, 1H, C*H*OH), 4.98 (d, ^3J = 7.2 Hz, 1H, $CHAr_2$), 4.15 (d, ^3J = 6.5 Hz, 1H, $CHAr_2$), 3.27 (td, $^3J \approx 7.1$, ^3J = 2.3 Hz, 1H, 9a-H), 1.75 (br s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 145.4 (s), 144.7 (s), 144.0 (s), 143.5 (s), 129.4 (d), 128.7 (d), 128.3 (d), 127.6 (d), 127.50 (d), 127.45 (d), 126.7 (d), 125.5 (d), 125.3 (d), 124.9 (d), 124.2 (d), 80.0 (d, CHOH), 64.9 (d), 54.7 (d), 53.3 (d). – MS, *m/z* (%): 298 (100) [$M^{\bullet+}$], 297 (6), 280 (39) [$M^{\bullet+}$ – H_2O], 279 (34), 278 (12), 277 (8), 276 (7), 269 (12), 268 (33), 267 (36), 266 (6), 265 (16), 253 (10), 252 (13), 221 (12), 220 (13), 219 (20), 207 (65), 203 (31), 202 (26), 194 (16), 193 (19), 192 (34), 191 (28), 189 (19), 178 (27), 166 (66), 165 (28), 152 (10), 131 (14), 118 (13), 115 (15), 107 (15), 105 (17), 91 (23), 77 (16).

(4bα,9aα)-9a-Benzyl-9a,10-dihydro-10α-phenylindeno[1,2-a]indene-(4bH)-one (**11**): A suspension of sodium hydride (300 mg, 12.5 mmol; 80% in paraffin) in 25 ml of dry 1,2-dimethoxyethane is magnetically stirred under nitrogen while a solution of **8** (2.96 g, 10.0 mmol) in the same solvent is injected through a rubber septum within 10 min. With continued stirring, the mixture is heated to 60°C (bath), then cooled to room temp., and a solution of benzyl bromide (1.71 g, 10.0 mmol) in 10 ml of 1,2-dimethoxyethane is added through the septum within 10 min. The mixture is heated to reflux for 40–50 h [with TLC control ($CHCl_3$)], then cooled and cautiously poured into 200 ml of water. After addition of diluted sulfuric acid to pH ≈ 5, the solution is extracted thrice with diethyl ether, and the combined extracts are washed with water and dried with Na_2SO_4. The solvent is evaporated to leave a light-brown, oily material which is purified by crystallization from ethanol to give **11** (2.40 g, 62%) as pale-yellow crystals; m.p. 164°C. (From runs on a 100-mmol scale, **11** is obtained in three crystal fractions; total yield 80%; m.p. 160–161°C). – IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1}, 3005, 2900, 1685, 1590, 1477, 1438, 750, 740, 690. – ^{1}H NMR (80 MHz): δ = 7.62 (d, ^3J = 7.3 Hz, 2H), 7.0–7.5 (m, 11H), 6.96 (s, 5H), 4.79 (s, 1H, $CHAr_2$), 4.75 (s, 1H, $CHAr_2$), AB spin system δ_A = 2.82, δ_B = 2.40 (^2J = –13.5 Hz, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 209.5 (s, C=O), 154.9 (s), 143.7 (s), 143.1 (s), 140.0 (s), 137.3 (s), 135.7 (s), 134.9 (d), 130.2 (d), 129.8 (d), 128.2 (d), 127.84 (d), 127.75 (d), 127.62 (d), 127.10 (d), 126.37 (d), 126.12 (d), 125.04 (d), 124.48 (d), 124.01 (d), 66.4 (s, C-9a), 56.8 (d, $CHAr_2$), 54.0 (d, $CHAr_2$), 39.3 (t, CH_2). – MS, *m/z* (%): 386 (6) [$M^{\bullet+}$], 295 (100) [$M^{\bullet+}$ – C_7H_7], 265 (16), 252 (7), 217 (21), 202 (6), 189 (9), 165 (9), 91 (27). – $C_{29}H_{22}O$ (386.5): calcd. C 90.12, H 5.74; found C 89.83, H 6.02.

(4bα,9aα)-9a-Benzyl-4b,9,9a,10-tetrahydro-10α-phenylindeno-[1,2-a]inden-9α-ol (**12**): To a stirred suspension of an excess of $LiAlH_4$ (380 mg, 10.0 mmol) in 5 ml dry tetrahydrofuran is added a solution of **11** (1.00 g, 2.60 mmol) in 20 ml of the same solvent. The mixture is heated to reflux for 3 h [TLC control ($CHCl_3$)], allowed to cool, and then carefully hydrolyzed with water and saturated aqueous NH_4Cl. After several extractions with diethyl ether, the combined extracts are dried with Na_2SO_4, and the solvent is evaporated to give a yellow, oily residue which is crystallized from petroleum ether/ethyl acetate (1:1) to yield **12** (760 mg, 75%) as pale-yellow crystals consisting of a single stereoisomer; m.p. 180°C. – IR (KBr): $\tilde{\nu}$ = 3540 cm^{-1}, 3040, 3000, 2920, 2890, 2865, 1580, 1050, 890, 770, 745, 720, 715, 695, 645. – ^{1}H NMR (300 MHz): δ = 7.05–7.37 (m, 13H), 6.84–6.96 (m, 5H), 5.17 (d, ^3J = 9.0 Hz, 1H, C*H*$^{\beta}$OH), 4.72 (s, 1H, 4b-H), 4.48 (s, 1H, 10-H), AB spin system δ_A = 2.83, δ_B = 2.51 (^2J = –14.1 Hz, 2H, CH_2), 1.91 (d, ^3J = 9.1 Hz, 1H, OH). – ^{13}C NMR (75 MHz): δ = 144.6 (s), 143.9 (s), 143.1 (s), 142.4 (s), 141.4 (s), 139.3 (s), 130.3 (d), 129.7 (d), 128.3 (d), 127.55 (d), 127.39 8d), 127.12 (d), 126.8 (d), 126.0 (d), 125.5 (d), 124.5 (d), 124.0 (d), 123.4 (d), 83.5 (d, CHOH), 66.6 (s, C-9a), 59.4 (d, $CHAr_2$), 56.2 (d, $CHAr_2$), 36.8 (t, CH_2). – MS, *m/z* (%): 388 (29) [$M^{\bullet+}$], 370 (55) [$M^{\bullet+}$ – H_2O], 297 (47), 296 (23), 295 (25), 279 (100), 278 (12), 265 (11), 252 (11), 219 (31), 204 (11), 203 (11), 193 (20), 191 (23), 189 (17), 178 (11), 167 (10), 165 (23), 91 (96). The assignments of the resonances of 4bα-H and 10β-H are based on ^{1}H-^{1}H COSY measurements (250 MHz) showing crosspeaks with the low- and high-field portions, respectively, of the arene proton multiplet at δ = 7.05–7.37, in close relation to the results obtained with the other diindans (Table 1). The corresponding ^{1}H-^{1}H NOESY measurements of **12** give a strong NOE of 9β-H on 10β-H, but none on 4bα-H. – $C_{29}H_{24}O$ (388.5): calcd. C 89.66, H 6.23; found C 89.44, H 6.26.

(4bα,8bβ)-4b,8b,13,14-Tetrahydro-13β-phenyldiindeno[1,2-a:2',1'-b]indene (**14**): Predried[38] ion exchange resin Amberlyst A-15 (50 mg, Fluka), is added to a solution of **12** (100 mg, 260 μmol) in 5 ml of dry benzene. The suspension is heated to reflux for 1 h, then allowed to cool, and the catalyst is filtered off and washed with some chloroform. The solvents are evaporated, and the solid residue is recrystallized from petroleum ether (30/70) to give **14** (90 mg, 93%) as a colorless crystal powder; m.p. 172°C. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3050, 3005, 2880, 1485, 1470, 1445, 768, 752, 743, 707, 697. – ^{1}H NMR (300 MHz): δ = 7.47 (d, ^3J = 7.5 Hz, 1H), 7.43 (dd, ^3J = 8.5, ^4J = 1.6 Hz, 1H), 7.0–7.37 (m, 15H), 4.62 (s, 1H, $CHAr_2$), 4.56 (s, 1H, $CHAr_2$), 4.55 (s, 1H, $CHAr_2$), AB spin system δ_A = 2.86, δ_B = 2.65 (^2J = –16.4 Hz, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 145.7 (s), 144.0 (s), 143.8 (s), 143.5 (s), 143.1 (s), 142.7 (s), 141.8 (s), 129.6 (d), 128.4 (d), 127.4 (d), 126.9 (d), 126.7 (d), 125.8 (d), 124.89 (d), 124.66 (d), 69.8 (s, C-13a), 61.2 (d, $CHAr_2$), 60.9 (d, $CHAr_2$), 57.2 (d, $CHAr_2$), 38.2 (t, CH_2). – MS, *m/z* (%): 370 (100) [$M^{\bullet+}$], 293 (15), 292 (26), 291 (17), 289 (10), 279 (21), 278 (7), 277 (6), 276 (6), 265 (4), 252 (3), 215 (10), 203 (5), 202 (8), 179 (6), 178 (9), 146 (10) [M^{2+} – C_6H_6]. – $C_{29}H_{22}$ (370.5): calcd. C 94.01, H 5.99; found C 94.13, H 6.14.

(4bα,9aα)-9a,10-Dihydro-10α-phenyl-9α-(phenylthio)indeno[1,2-a]inden-9(4bH)-one (**21**): A reaction apparatus assembled from predried glassware and equipped with a rubber septum is flushed with dry nitrogen. After introduction of 100 ml of dry tetrahydrofuran and 15.0 ml (110 mmol) of freshly distilled diisopropylamine, the resulting solution is cooled to –60°C by means of dry ice/acetone. Within 30 min, 80 ml of a 1.5 M solution of *n*-butyllithium (120 mmol) in *n*-hexane is added through the septum. The mixture is stirred and allowed to warm to 0°C. The stirred solution of lithium diisopropylamide thus prepared is recooled to –45°C, and a solution of **8** (30.0 g, 101 mmol) in 150 ml of dry tetrahydrofuran is added through the septum within 40 min. Stirring is continued while the mixture is allowed to warm to 0°C within 1 h, its color turning from yellow to dark brown. While the temperature is being maintained by using an ice/water bath, a solution of 24.0 g (110 mmol) of diphenyl disulfide in 75 ml of dry tetrahydrofuran is injected within 20 min. Finally, the mixture is allowed to warm to room temp. and then stirred for further 1.5 h. The green solution is poured on 100 ml of a mixture of diluted hydrochloric acid and tetrahydrofuran (ca. 10:1). The organic layer is washed with diluted hydrochloric acid, turning orange, and then twice with saturated aqueous $NaHCO_3$, water, and dried with sodium sulfate. Evaporation of the solvent gives a solid residue, which is recrystallized from petroleum ether/ethyl acetate yielding **21** (32.0 g, 78%) as a colorless crystalline powder; m.p. 171–172°C. – IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1}, 3025, 3000, 2900, 1700, 1590, 770, 755, 745, 740, 695, 690, 660, 610. – ^{1}H NMR (80 MHz): δ = 6.8–7.65 (m, 18H), 4.97 (s, 2H, 2 $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 204.1 (s, C=O), 153.8 (s), 143.9 (s), 142.3 (s), 140.0 (s), 136.1 (d), 135.2 (d), 134.8 (s), 130.5 (d), 128.8 (d), 128.26 (d), 128.16 (d), 127.99 (d), 127.86

(d), 127.45 (d), 126.2 (d), 124.82 (d), 124.72 (d), 124.1 (d), 70.9 (s, C-9a), 58.6 (d, $CHAr_2$), 55.7 (d, $CHAr_2$). – MS, *m/z* (%): 404 (50) [$M^{\bullet+}$], 295 (100) [$M^{\bullet+}$ – PhS], 294 (73), 265 (34), 263 (10), 252 (9), 239 (5), 217 (18), 189 (13), 165 (8), 163 (4), 109 (20). – $C_{28}H_{20}OS$ (404.5): calcd. C 83.14, H 4.98; found C 82.70, H 5.29.

(4ba,9aa)-9a,10-Dihydro-10a-phenyl-9a-(phenylsulfinyl)indeno-[1,2-a]inden-9(4bH)-one (**22**): A stirred solution of **21** (27.0 g, 66.8 mmol) in 500 ml of distilled dichloromethane is cooled to −30°C, and a solution of 14.5 g of *meta*-chloroperbenzoic acid (67 mmol; Janssen, 80% purity) in 200 ml of the same solvent is added within 45 min. The mixture is allowed to warm to room temp. and stirred for 15 h [TLC control ($CHCl_3$)]. It is then poured on 400 ml of diethyl ether and 400 ml of aqueous Na_2SO_3 (10%), and the aqueous layer is extracted with ether. The combined organic solutions are washed twice with aqueous $NaHCO_3$, then water, and are dried with Na_2SO_4. The solvent mixture is evaporated and the solid recrystallized from petroleum ether/ethyl acetate (1:1) to give **22** (23.8 g, 85%) as almost colorless crystals; m.p. 160.5–161°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3020, 2900, 1685, 1590, 1048, 763, 743, 700, 690. – ^1H NMR (80 MHz): δ = 7.55 (d, $^3J \approx 7.5$ Hz, 1H), 6.9–7.6 (m, 18H), 5.67 (s, 1H, $CHAr_2$), 5.35 (s, 1H, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 201.6 (s, C=O), 156.1 (s), 143.2 (s), 142.2 (s), 139.2 (s), 138.2 (s), 135.5 (d), 135.0 (s), 131.3 (d), 128.2 (d), 128.1 (d), 128.0 (d), 126.2 (d), 125.8 (d), 124.7 (d), 124.5 (d), 124.3 (d), 86.5 (s, 9a-C), 56.0 (d), 47.7 (d). – MS, *m/z* (%): 295 (100) [$M^{\bullet+}$ – PhSO], 294 (82), 293 (17), 265 (48), 263 (20), 252 (7), 218 (14), 217 (15), 189 (13), 165 (4), 132 (10), 126 (19), 125 (15), 109 (25), 78 (38). – $C_{28}H_{20}O_2S$ (420.5): calcd. C 79.97, H 4.79; found C 79.86, H 5.01.

This reaction is performed in batches up to the 60-g scale of **21**. Varying effective amounts of MCPBA are used, which occasionally requires the addition of supplementary reagent to complete the oxidation. In most cases, the formation of a byproduct, viz. sulfone **23** (see below), is observed. The combined yields of **22** and **23** have been found to be as high as 94%. The sulfone is separated upon the recrystallization of **22** described above. Advantageously, however, the sulfoxide **22** containing up to 10% of **23** can be employed in the thermal elimination to form the enones **15** and **16**.

(4ba,9aa)-9a,10-Dihydro-10a-phenyl-9a-(phenylsulfonyl)indeno-[1,2-a]inden-9(4bH)-one (**23**): From the oxidation **21** → **22** described above, varying amounts of a material of low solubility in petroleum ether/ethyl acetate may be isolated. Recrystallization from ethyl acetate/tetrahydrofuran (ca. 3:2) gives colorless crystals which are identified as the sulfone **23**; m.p. 207°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 3023, 2920, 1703, 1604, 1454, 1443, 1286, 1265, 1247, 1194, 1181, 1084, 1032, 938, 757, 724, 696, 617. – ^1H NMR (300 MHz): δ = 7.25–7.40 (m, 11H), 7.10–7.20 (m, 2H), 7.00–7.10 (m, 5H), 5.31 (s, 1H, $CHAr_2$), 4.82 (s, 1H, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 197.6 (s, C=O), 153.2 (s), 144.1 (s), 141.3 (s), 139.6 (s), 139.4 (s), 136.2 (s), 134.8 (d), 131.5 (d), 130.6 (d), 128.5 (d), 128.4 (d), 128.2 (d), 128.0 (d), 127.8 (d), 127.7 (d), 126.2 (d), 125.5 (d), 124.4 (d), 124.2 (d), 82.3 (s, 9a-C), 54.5 (d), 51.7 (d). – MS, *m/z* (%): 436 (≈0.5) [$M^{\bullet+}$], 295 (100) [$M^{\bullet+}$ – $PhSO_2$], 294 (18), 265 (30), 263 (11), 252 (11), 239 (5), 218 (17), 217 (18), 193 (5), 189 (14), 165 (8), 125 (7), 97 (5). This compound has been found to decompose readily on standing; satisfying combustion analytical data have not been obtained; exact mass measurements give: calcd. 436.1133; found 436.1180.

(4ba,9aa)-9a,10-Dihydro-10a-phenyl-9a-(phenylseleno)indeno-[1,2-a]inden-9(4bH)-one (**24**): A solution of lithium diisopropylamide (11.0 mmol) in tetrahydrofuran is prepared as described above. The solution is stirred and cooled to −40°C, and a solution of **8** (2.96 g, 10.0 mmol) in 10 ml of dry tetrahydrofuran is added through the rubber septum within 10 min. After stirring at −40°C for 30 min, a solution of 2.36 g (11.0 mmol) of benzeneselenyl bromide in 10 ml of tetrahydrofuran is added. The mixture is stirred for another 30 min and then poured on 50 ml of 0.5 N aqueous HCl and 50 ml of diethyl ether. The aqueous layer is extracted with diethyl ether, and the combined organic solutions are washed with aqueous $NaHCO_3$ and dried with Na_2SO_4. The solvents are evaporated to give a red-brown oily residue which is crystallized from petroleum ether/ethyl acetate to yield **24** (2.90 g, 64%) as pale-pink crystals; m.p. 169–170°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3000, 2900, 1695, 1590, 780, 760, 752, 734, 720, 695, 686, 610. – ^1H NMR (80 MHz): δ = 6.75–7.8 (m, 18H), 5.06 (s, 1H, $CHAr_2$), 5.00 (s, 1H, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 204.7 (s, C=O), 154.0 (s), 143.9 (s), 142.8 (s), 141.3 (s), 137.4 (d), 134.9 (d), 135.2 (s), 130.0 (d), 128.8 (d), 128.27 (d), 128.10 (d), 128.03 (d), 127.87 (d), 127.79 (d), 127.50 (d), 126.2 (d), 124.58 (d), 123.90 (d), 66.7 (s, C-9a), 59.7 (d, $CHAr_2$), 55.4 (d, $CHAr_2$). – MS, *m/z* (%): 452 (7) [[^{80}Se]$M^{\bullet+}$], 295 (100) [$M^{\bullet+}$ – PhSe], 294 (47), 293 (17), 280 (24), 279 (22), 278 (12), 267 (14), 265 (23), 252 (14), 219 (18), 218 (19), 191 (14), 189 (27), 165 (17), 157 (12) [$Ph^{80}Se^+$]. – $C_{28}H_{20}OSe$ (451.4): calcd. C 74.50, H 4.47; found C 74.45, H 4.85.

(4ba,9aa)-9a,10-Dihydro-10a-phenyl-9a-(phenyseleninyl)indeno-[1,2-a]inden-9(4bH)-one (**25**): A solution of **24** (1.00 g, 2.21 mmol) in 30 ml of distilled dichloromethane is stirred and cooled to −30°C unter nitrogen, and a solution of 520 mg of *meta*-chloroperbenzoic acid (2.4 mmol; Janssen, purity 80%) in the same solvent is added. The mixture is allowed to warm to room temp. and is then stirred for further 10 h [TLC control ($CHCl_3$)]. It is then poured on 50 ml of diethyl ether and 50 ml of aqueous Na_2SO_3 (10%). The aqueous layer is extracted with diethyl ether, and the combined organic solutions are washed with $NaHCO_3$ and dried with Na_2SO_4. The solvents are removed in vacuo at room temp. to prevent decomposition of the product, and the oily residue is subjected to liquid chromatography (CH_2Cl_2) to give **25** (0.48 g, 46%) as yellow-orange crystals; m.p. 138°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3010, 1675, 1585, 938, 780, 760, 752, 738, 730, 700. – ^1H NMR (300 MHz): δ = 7.8–7.95 (m, 2H), 7.15–7.6 (m, 16H), 4.95 (s, 2H, 2 $CHAr_2$). – MS, *m/z* (%): 294 (100) [$M^{\bullet+}$ – PhSeO], 293 (22), 265 (70), 263 (41), 239 (11), 189 (12), 187 (10), 163 (5), 147 (8), 133 (16), 132 (25). This compound has been found to decompose readily on standing; satisfying combustion analytical data have not been obtained.

10-Phenylindeno[1,2-a]inden-9(10H)-one and 10-Phenylindeno-[1,2-a]inden-9(4bH)-one (as a mixture, **15** and **16**)

a) The method described previously[2] using bromine vapors in dry air (or nitrogen) has been modified in various ways. In our laboratory, the best results have been obtained as follows: A stream of dry nitrogen is slowly bubbled through a solution of 0.30 ml (5.9 mmol) of bromine in 200 ml of dry chloroform (Merck, p.a.) and then through a solution of **8** (3.00 g, 10.0 mmol) in 170 ml of the same solvent. The stream is maintained for a total of 95 h while the progress of the reaction is followed by TLC (CH_2Cl_2), and additional bromine (4 × 0.2 ml) in chloroform is used. The yellow solution is concentrated to a small volume, and 15 ml of diethyl ether is added. A crystalline product may precipitate but is redissolved by addition of some tetrahydrofuran, and the solution is eluted twice through alumina (diethyl ether as eluent). After concentration of the combined eluates to a volume of ca. 40 ml, the solution is kept at 0–5°C to give a mixture of **15/16** as yellow crystals (0.25 g, 8.4%), m.p. 265–273°C (dec.).

b) An upscaled procedure omitting the tedious use of bromine vapors is given in the following: To a solution of 5.0 g (17.0 mmol)

of **8** in 200 ml of chloroform (Merck, p.a.) is added 120 g of finely powdered, dry potassium carbonate. The suspension is vigorously stirred, and a solution of bromine (3.5 ml, 69 mmol) in 200 ml of chloroform (p.a.) is added within 5 h. The color of the solution turns yellow-orange and should be maintained throughout the addition. After stirring overnight, the suspension is filtered, and the salts are washed with chloroform. The lemon-yellow solution is concentrated to a volume of 10 ml and, after dilution with 40 ml of diethyl ether, is eluted through neutral alumina (act. grade I/90, 10–15% water, column 2 · 30 cm) with diethyl ether. The resulting eluate is concentrated to ca. 75 ml and kept at 0–5°C for 3 d. The fine, yellow precipitate is collected, representing a mixture [TLC (CH_2Cl_2, R_f = 0.16 and 0.18] of **15** and **16** (0.5 g, 10%) as a bright-yellow powder, m.p. 260–278°C (dec.). The mother liquor is eluted through alumina for another time to give a further crop of **16/17** (0.25 g; total yield 15%).

c) *Thermal syn Elimination with* **22**: The procedure described in the following has been upscaled to 50-g batches with similar results. A mixture of 16.0 g (38.1 mmol) of **22** and 600 ml of freshly distilled toluene is heated to reflux for 4 d. The initally clear, orange solution turns yellow within some hours, and the course of the reaction is followed by TLC ($CHCl_3$). The solvent is evaporated to give an orange-red, oily residue which is redissolved with ca. 90 ml of chloroform, and petroleum ether (ca. 400 ml) is added in small portions to precipitate a fine-crystalline, yellow material. The mixture is cooled to 0–5°C for 3 h, and the precipitate is then filtered by suction, washed with some petroleum ether, and dried to give a yellow powder (8.2 g). TLC analysis (CH_2Cl_2 or $CHCl_3$) of this material shows two yellow components ($R_f \approx 0.1$ and 0.15) and an orange, less polar component. The mixture is digested several times with benzene to remove the orange, less polar component, giving a mixture of **15** and **16** as lemon-yellow crystals (5.8 g, 52%); m.p. 267–268°C (dec.). Baker et al.[2] reported m.p. 266–269°C. Repeated recrystallization of this mixture from benzene or toluene gives a yellow material containing almost exclusively the slowly eluting component ($R_f \approx 0.18$, $CHCl_3$); m.p. 281–282°C (dec.), which is poorly soluble in hot toluene. Workup of the mother liquors gives a yellow material containing almost exclusively the faster eluting compound ($R_f \approx 0.27$, $CHCl_3$); m.p. 236–240°C (decomp.). The **15/16** mixture may also be recrystallized from dichloromethane; both components undergo hydrogenation to **20**. – Liquid column chromatography (CH_2Cl_2/Kieselgel 60; Merck) of the mixture obtained after digestion of the crude precipitate with benzene also allows removal of all byproducts; a separation of **15** and **16**, however, is not achieved.

d) *Thermal syn Elimination with* **23**: In a way analogous to that described above for **22**, a mixture of **15** and **16** is obtained by heating 3.0 g (6.9 mmol) of **23** in 100 ml of toluene. However, the reaction requires 6–7 d to be completed, yielding **15/16** (750 mg, 37%).

e) *Thermal syn Elimination with* **25**: In an analogous procedure, the selenium oxide **25** (32.2 g, 68.9 mmol) is heated in 1.5 l of toluene for 7 d. Precipitation of the crude product mixture with petroleum ether followed by digestion with benzene gives a mixture of **15** and **16** (8.0 g, 39%); m.p. 281–282°C. – IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1}, 1692 (C=O), 1602, 1589, 1556, 1490, 1463, 1443, 778, 746 (s), 736 (s), 703 (s), 695 (s), 662, 632, 614. – ^1H NMR (300 MHz, $CDCl_2CDCl_2$): δ = 8.23 (d, ^3J = 7.5 Hz, 1H), 8.11 (d, ^3J = 7.6 Hz, 1H), 7.73 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1H) 7.17–7.7 (m, ca. 20H), 7.12 (quasi-t, ^3J = 7.8 Hz, 3H). – ^{13}C NMR (75 MHz): δ = 183.7 and 183.4 (s, C=O), 151.0 and 150.1 (s, C^{Ar}–CO), 147.7 (s), 146.0 (s), 145.5 (s), 144.7 (s), 144.4 (s), 144.2 (s), 143.3 (s), 143.0 (s), 133.1 (d), 132.5 (d), 130.8 (s), 130.6 (d), 130.3 (d), 130.0 (d), 129.0 (d), 128.8 (d), 128.7 (d), 128.5 (d), 128.1 (d), 128.0 (d), 127.7 (d), 125.7 (d), 125.4 (d), 124.6 (d), 124.3 (d), 122.7 (d), 68.89 and 68.78 (s, $CHAr_2$). – MS, *m/z* (%): 294 (31) [$M^{\bullet+}$], 293 (100), 265 (10), 264 (10), 263 (36), 261 (9), 239 (4), 237 (5). – $C_{22}H_{14}O$ (294.4): calcd. C 89.77, H 4.79; found C 88.99, H 4.93.

2-Bromo-2-(α-bromobenzyl)-2,3-dihydro-3-phenyl-1H-inden-1-one (**19**)

a) *By Treatment of* **8** *with an Excess of Bromine Vapor:* A slow steam of dry nitrogen is bubbled through a solution of 0.2 ml (7.7 mmol) of bromine in 70 ml of chloroform (p.a.) and then through a solution of 1.00 g (3.37 mmol) of **8** in 70 ml of the same solvent. After 14 h, the color of the reagent solution has vanished almost completely. The reaction mixture is concentrated to dryness, and the residue is subjected to chromatography (Kieselgel, CH_2Cl_2) to give ca. 0.6 g (60%) of the starting material and a second fraction, which is recrystallized from CH_2Cl_2/ethanol to give **19** (100 mg, 6%) as colorless crystals; m.p. 134–138°C (decomp.).

b) *By Addition of Bromine to* **7**: To a stirred suspension of 2.96 g (10.0 mmol) of **7** in 75 ml of dry tetrachloromethane is added 1.60 g (10.0 mmol) of bromine in 25 ml of the same solvent within 1 h, and stirring is continued overnight to give a clear solution. Evaporation of the solvent and twofold recrystallization from petroleum ether/ethyl acetate give the dibromo adduct **19** (3.70 g, 81%) as large, colorless crystals; m.p. 141–147°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3064, 3035, 2967, 2897, 1719 (C=O), 1604, 1493, 1462, 1448, 1288, 1277, 1262, 1211, 1150, 1024, 1014, 756 (s), 702 (s). – ^1H NMR (300 MHz): δ = 7.95 (d, ^3J = 7.7 Hz, 1H), 7.74 (dd, ^3J = 7.5, ^4J = 1.8 Hz, 2H), 7.64 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 7.48 (t, ^3J = 7.4 Hz, 1H), 7.32–7.40 (m, 3H), 7.20 (d, ^3J = 7.4 Hz, 1H), 7.06–7.14 (m, 3H), 6.78 (dd, ^3J = 7.8, $^4J \approx$ 1.7 Hz, 2H), 5.87 (s, 1H), 5.50 (s, 1H). – ^{13}C NMR (75 MHz): δ = 198.6 (s, C=O), 154.4 (s), 140.5 (s), 136.3 (d), 135.7 (s), 133.4 (s), 130.8 (d), 129.1 (d), 128.7 (d), 127.80 (d), 127.51 (d), 127.38 (d), 127.1 (d), 124.9 (d), 72.6 (s, C-2), 57.0 (d), 51.0 (d). – MS, *m/z* (%): 454/456/458 (0.3/0.6/0.3) [$M^{\bullet+}$], 375/377 (30/30) [$M^{\bullet+}$ – Br], 296 (83) [$M^{\bullet+}$ – 2 Br], 295 (100) [$M^{\bullet+}$ – (Br, HBr)], 279 (10), 268 (20), 267 (25), 265 (27), 252 (19), 239 (7), 219 (15), 218 (22), 217 (9), 191 (19), 189 (30), 169/171 (14/14) [$C_7H_6Br^+$], 165 (27). – $C_{22}H_{16}Br_2O$ (456.2): calcd. C 57.93, H 3.54; found C 58.42, H 3.63.

(4ba,9aa)-9a,10-Dihydro-10β-phenylindeno[1,2-a]inden-9(4bH)-one (**20**): A suspension of 1.5 g of palladium-on-charcoal (10%, Merck) in 450 ml of dioxane (freshly distilled from $LiAlH_4$) is shaken under hydrogen in a hydrogenation apparatus for 2 h (ca. 50 ml of H_2 being absorbed). After flushing with inert gas, 10.4 g (35.3 mmol) of **15/16** is added, and the yellowish suspension (!) is shaken under hydrogen gas (1 bar) until 940 ml (ca. 110%) of H_2 has been absorbed. The homogeneous and almost colorless solution is filtered (**caution!**), the catalyst is washed with some dioxane and the solvent evaporated to give an yellowish, oily residue. TLC control (CH_2Cl_2) shows complete conversion of the starting material. Redissolution of the residue in methanol and cooling to –15°C afford a very loose gel which is quickly filtered by suction through a precooled Buchner funnel and dried in vacuo to give a light-brown powder. Further material may be collected in the same way from the mother liquors to give crude **20** [total yield 7.4 g (71%). In a series of runs, yields range from 60–83%]. Further purification of this material by flash chromatography (silica gel, CH_2Cl_2) followed by recrystallization from *n*-hexane/$CHCl_3$ (ca. 12:1) gives colorless crystals; m.p. 77–80°C. – IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 3031, 2956, 2930, 2894, 2873, 1702, 1604, 1582, 786, 759, 705, 642, 614, 605. – ^1H NMR (300 MHz): δ = 7.77 (d, ^3J = 7.7 Hz, 1H),

7.66 (d, ^3J = 7.6 Hz, 1H), 7.59 (t, ^3J = 7.4 Hz, 1H), 7.45 (d, ^3J = 7.6 Hz, 1H), 7.05–7.32 (m, 7H), 6.93 (d, ^3J = 7.6 Hz, 1H), ca. 6.74 (br m, 2H), 4.97 (d, ^3J = 7.3 Hz, 1H, $CHAr_2$), 4.94 (d, ^3J = 11.7 Hz, 1H, $CHAr_2$), 3.91 (dd, ^3J = 7.4, ^3J = 11.7 Hz, 1H, 9a-H). – ^{13}C NMR (75 MHz): δ = 205.1 (s, C=O), 156.1 (s), 145.6 (s), 143.1 (s), 141.4 (s), 137.4 (s), 134.9 (d), 129.5 (d), 127.9 (d), 126.8 (d), 126.3 (d), 125.3 (d), 124.2 (d), 123.8 (d), 55.6 (d), 52.9 (d), 51.0 (d). – MS, *m/z* (%): 296 (100) [$M^{\bullet+}$], 295 (21), 279 (13), 278 (10), 267 (15), 265 (20), 252 (15), 239 (5), 219 (14), 218 (16), 194 (6), 191 (13), 189 (17), 165 (13). – $C_{22}H_{16}O$ (296.4): calcd. C 89.16, H 5.44; found C 88.97, H 5.83.

(4ba,9aa)-4b,9,9a,10-Tetrahydro-10β-phenylindeno[1,2-a]inden-9β-ol (**27**): To a stirred solution of $LiAlH_4$ (190 mg, 5.0 mmol) in dry diethyl ether is added a solution of **20** (3.0 g, 10.0 mmol) in 100 ml of diethyl ether. The mixture is heated to reflux for 3 h; TLC control (CH_2Cl_2, $R_f \approx 0.6$) shows that, apparently, only one product is formed. The mixture is cooled to 0°C and carefully hydrolyzed with ice water. After addition of aqueous NH_4Cl, the aqueous layer is extracted with diethyl ether, and the combined organic solutions are washed with water and dried with Na_2SO_4. Evaporation of the solvent, eventually in vacuo (100°C, 0.1 mbar) furnishes a yellowish residue, which is further purified by column chromatography ($CHCl_3$) to give **27** (3.0, ca. 100%) as a colorless, glassy material. All attempts to crystallize the alcohol have been unsucessful; the crude material, however, may be used in the final cyclization step (see below). – IR (KBr): $\tilde{\nu}$ = 3564 cm^{-1} (sh, OH), 3457 (br, OH), 3067, 3028, 2932, 2885, 1597, 1493, 1473, 1452, 1400, 1110, 1089, 1046, 1020, 753, 700. – ^1H NMR (300 MHz): δ = 7.56 (d, ^3J = 7.4 Hz, 1H), 7.45 (d, ^3J = 7.4 Hz, 1H), 7.27 and 7.25 (two d, $^3J \approx 7.4$ Hz, 2H), 7.18 (t, ^3J = 7.3 Hz, 2H), 7.0–7.15 (m, 5H), 6.81 (dd, ^3J = 7.7, $^4J \approx 1.5$ Hz, 2H), 5.24 [br t (D_2O: d), ^3J = 7.0 Hz, 1H, C*H*OH), 4.80 (d, ^3J = 9.2 Hz, 1H), 4.61 (d, ^3J = 7.2 Hz, 1H), 3.85 (dt, $^3J \approx 9.2$, ^3J = 7.2 Hz, 1H, 9a-H), 1.3 (br s, 1H, OH). – ^{13}C NMR (75 MHz): δ = 146.4 (s), 145.7 (s), 144.7 (s), 143.0 (s), 129.8 (d), 128.1 (d), 127.31 (d), 127.09 (d), 126.6 (d), 125.3 (d), 124.15 (d), 124.05 (d), 123.5 (d), 77.2 (d, CHOH), 53.9 (d), 53.3 (d), 52.1 (d). – MS, *m/z* (%): 298 (98) [$M^{\bullet+}$], 297 (20), 280 (100) [$M^{\bullet+} - H_2O$], 279 (48), 278 (11), 277 (9), 276 (6), 269 (6), 267 (9), 265 (29), 254 (12), 253 (17), 252 (18), 221 (43), 220 (32), 218 (11), 207 (20), 203 (57), 202 (30), 194 (11), 193 (11), 192 (25), 191 (22), 190 (12), 189 (25), 179 (13), 178 (28), 167 (21), 165 (34), 152 (9), 131 (9), 115 (16), 105 (23), 91 (29). – $C_{22}H_{18}O$ (298.4): calcd. C 88.46, H 6.08; found C 88.06, H 6.36. – calcd. 298.1358; found 298.1354 (MS).

Attempted synthesis of (4ba,9aa)-4b,9,9a,10-Tetrahydro-10β-phenylindeno[1,2-a]inden-9a-ol (**26**): To a solution of $Al(OiPr)_3$ (0.8 g) in 15 ml of 2-propanol is slowly added a solution of **20** (0.70 g, 2.4 mmol) in 25 ml of dry toluene. The mixture is heated under the same conditions used for the reduction of the 10α-phenyl isomer (**8** → **10**, see above). No reaction is observed after a total of 30 h, whereas **8** (100 mg), added for control purposes, does react to furnish **10** (TLC control). Heating to reflux after exchange of the toluene for xylene and addition of further 0.4 g of the reagent is also non-productive; workup and ^1H-NMR analysis reveal essentially unchanged starting ketone **20**.

(4ba,8ba,12ba,12da)-4b,8b,12b,12d-Tetrahydrodibenzo[2,3:4,5]-pentaleno[1,6-ab]indene, Tribenzotriquinacene (**4**): A mixture of orthophosphoric acid (85%, 0.4 ml) and 100 ml of toluene is heated in a water separator for 2 h. After cooling to ca. 60°C, **27** (3.0 g, 10 mmol) is added, and heating is continued for 18 h with vigorous stirring. The product may precipitate partially from the hot reaction mixture and, upon cooling to room temp., readily crystallizes quantitatively as fine, colorless needles. The crystals are collected by suction and washed with some cold ethanol to give **4** (1.6 g, 57%) which may be recrystallized from 200 ml (!) of hot xylene to furnish the hydrocarbon as thin and long, colorless needles; m.p. 390–391°C. All spectroscopic data are identical with those published previously (see refs.[4,31] and discussion). – Alternatively, the dehydration may be carried out by heating of a solution of **27** (1.90 g, 6.4 mmol) in 100 ml of benzene with 0.6 g of Amberlyst A-15 for 3 h. The product starts precipitating after 5–10 min; workup and recrystallization from xylene give **4** (1.05 g, 59%).

(4ba,9aa)-4b,9,9a,10-Tetrahydro-9a-phenylindeno[1,2-a]indene (**28**): A solution of 2.96 g (10.0 mmol) of **8** in 100 ml of ethanol is shaken with 0.3 g of Pd/C (10%, Merck) at 50°C under hydrogen (5 bar) for 12 h. Workup of the cooled reaction mixture and recrystallization of the crude product from ethanol gives **28** (2.26 g, 80%) as colorless crystals; m.p. 109–110°C. This hydrocarbon has been obtained previously by Wolff-Kishner reduction of **8**, m.p. 112°C[2]. – IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1}, 3027, 2975, 2939, 2905, 2860, 2844, 1596, 1583, 1491, 1470, 1452, 1440, 802, 761, 741, 713, 689, 627, 610. – ^1H NMR (300 MHz): δ = 7.53 (d, ^3J = 7.4 Hz, 1H), 7.10–7.38 (m, 11H), 6.85 (d, ^3J = 7.5 Hz, 1H), 4.78 (d, ^3J = 7.6 Hz, 1H, $CHAr_2$), 4.02 (d, ^3J = 7.1 Hz, 1H, $CHAr_2$), 3.38 (qt, $^3J \approx 7.5$, $^3J_{(AM)}$ = 2.5 Hz, 1H, 9a-H), ABM spin system δ_M = 3.38, δ_B = 3.21, δ_A = 3.01 ($^2J_{AB}$ = –16.2, $^3J_{AM}$ = 2.4, $^3J_{BM}$ = 7.7 Hz, 3H, CH_2, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 146.3 (s), 144.92 (s), 144.87 (s), 143.5 (s), 142.4 (s), 128.6 (d), 128.4 (d), 127.16 (d), 127.10 (d), 126.84 (d), 126.76 (d), 126.5 (d), 125.1 (d), 124.5 (d), 124.0 (d), 57.7 (d), 55.6 (d), 54.8 (d), 37.1 (t). – MS, *m/z* (%): 282 (67) [$M^{\bullet+}$], 281 (9), 280 (6), 278 (3), 277 (4), 276 (4), 267 (5), 266 (5), 265 (11), 252 (7), 239 (4), 205 (7), 204 (13), 203 (25), 202 (19), 191 (100), 167 (13), 165 (10). – $C_{22}H_{18}$ (282.4): calcd. C 93.58, H 6.42; found C 93.24, H 6.53.

(4ba,9aa)-4b,9,9a,10-Tetrahydro-9β-phenylindeno[1,2-a]indene (**29**): A solution of 0.20 g (670 μmol) of **20** in 40 ml of ethanol is shaken with 0.1 g of Pd/C (10%, Merck) at 55°C under hydrogen (5 bar) overnight. Workup of the cooled reaction mixture followed by kugelrohr distillation (220°C/0.1 mbar) of the crude product and recrystallization from ethanol give **29** (0.14 g, 74%) as colorless crystals; m.p. 81–82°C. – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3019, 2960, 2931, 2895, 2861, 2839, 1603, 1577, 1491, 1475, 1450, 1431, 1392, 799, 761, 750, 729, 719, 703, 687, 672, 610. – ^1H NMR (300 MHz): δ = 7.51 (d, ^3J = 7.4 Hz, 1H), 7.41 (d, ^3J = 6.9 Hz, 1H), 7.13–7.33 (m, 9H), 7.09 (t, ^3J = 7.3 Hz, 1H), 6.96 (d, ^3J = 7.4 Hz, 1H), 4.78 (d, ^3J = 8.2 Hz, 1H, $CHAr_2$), 4.69 (d, ^3J = 7.6 Hz, 1H, $CHAr_2$), 3.69 (quint, $^3J \approx 8.1$ Hz, 1H, 9a-H), ABX spin system δ_X = 3.69, δ_B = 2.59, δ_A = 2.52 ($^2J_{AB}$ = –16.6, $^3J_{AX}$ = 9.0, $^3J_{BX}$ = 7.9 Hz, 3H, CH_2, $CHAr_2$). – ^{13}C NMR (75 MHz): δ = 144.9 (s), 144.6 (s), 144.1 (s), 143.5 (s), 141.6 (s), 129.2 (d), 128.1 (d), 127.1 (d), 126.85 (d), 126.77 (d), 126.4 (d), 125.9 (d), 124.6 (d), 124.4 (d), 123.8 (d), 55.5 (d), 53.2 (d), 49.7 (d), 34.0 (t). – MS, *m/z* (%): 282 (100) [$M^{\bullet+}$], 281 (21), 280 (8), 279 (6), 267 (9), 266 (6), 265 (12), 252 (6), 205 (16), 204 (36), 203 (33), 202 (11), 191 (71), 178 (8), 167 (44), 165 (7). – $C_{22}H_{18}$ (282.4): calcd. C 93.58, H 6.42; found C 93.47, H 6.65.

9,10-Dihydro-10-phenylindeno[1,2-a]indene (**30**)

a) *By dehydration of* **9** *and* **27** *with DMSO:* A solution of 0.50 g (1.68 mmol) of **9** (or the stereoisomer **27**) in 5.0 ml of freshly distilled dimethyl sulfoxide is heated under nitrogen at 175°C for 6 h. The mixture is allowed to cool under nitrogen, diluted with 10 ml of water and extracted with *n*-hexane. The extract is washed with water and dried with Na_2SO_4. Evaporation of the solvent gives an oily residue which is subjected to MPLC (Kieselgel 60/chloroform)

to give 95–115 mg (20–25%) of a colorless oil. Both in the case of **9** and **27**, the ^{1}H-NMR spectra of the products are identical with those of the crystalline product described below.

b) *By Cyclodehydration of 2-Benzhydryl-1,3-indandiol:* As described recently[2], a mixture of 10.5 g (33.0 mmol) of **34**, 80 ml of chlorobenzene, and 5.0 ml of orthophosphoric acid (85%) is allowed to react at 120°C (bath temp.) for 20 h. The readily crystallizing **4** is quantitatively separated by filtration (yield 11%[2]), and the filtrate is concentrated to give a yellow oil. Kugelrohr distillation (170–190°C, 0.1 mbar) followed by recrystallization from ethanol gives **30** (2.80 g, 30%); m.p. 185°C. – IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 3028, 2902, 2886, 2768, 1599, 1491, 1479, 1451, 1395, 772, 757, 739, 728, 713, 701, 643, 609. – ^{1}H NMR (300 MHz): δ = 7.78 (d, ^3J = 7.5 Hz, 1H), 7.75 (d, ^3J = 7.5 Hz, 1H), 7.48 (d, ^3J = 7.4 Hz, 1H), 6.10–7.40 (m, 8H), 7.10 (dd, ^3J = 7.8, ^4J ≈ 1.6 Hz, 2H), 4.79 (s, 1H, $CHAr_2$), AB spin system δ_A = 3.51, δ_B = 3.42 (^2J = −23.4 Hz, 2H, CH_2). – ^{13}C NMR (75 MHz): δ = 157.9 (s), 152.8 (s), 148.0 (s), 147.5 (s), 140.0 (s), 139.3 (s), 138.7 (s), 128.8 (d), 127.9 (d), 126.89 (d), 126.84 (d), 126.54 (d), 125.06 (d), 124.77 (d), 124.69 (d), 119.91 (d), 119.65 (d), 53.1 (d, C-4b), 34.5 (t, C-9). – MS, *m/z* (%): 280 (100) [M$^{\bullet+}$], 279 (44), 278 (12), 277 (10), 276 (14), 265 (5), 263 (3), 252 (6), 203 (53), 202 (47), 201 (5), 200 (7), 178 (6), 139 (8), 138 (12). – $C_{22}H_{16}$ (280.4): calcd. C 94.25, H 5.75; found C 94.13, H 5.95.

The ^{1}H-^{1}H COSY spectrum of **30** allows us to distinguish between this olefin and the isomer **32** in the following way: The two low-field arene doublets at δ = 7.78 and 7.75 are assigned to 4-H and 5-H, in parallel to the features of many other diindan derivatives presented in this work. Correspondingly, the high-field arene double doublet at δ = 7.10 is attributed to the *ortho*-protons of the phenyl group. The benzhydrylic methine singlet (δ = 4.79) clearly shows crosspeaks with only one of the low-field arene signals (viz. that at δ = 7.78), and, in addition, with the low-field signal at δ = 7.10. In turn, the methylene AB system (δ = 3.51 and 3.42) exhibits only one characteristic crosspeak with just the other low-field doublet (δ = 7.75). This clearly rules out the presence of a "quasi-symmetrical" methine proton at C-4b anticipated for **32** but is in full accordance with the structure of **30**.

☆ Dedicated to Professor *Eckehard V. Dehmlow* on the occasion of his 60th birthday.

[1] [1a] 13. Communication: R. Eckrich, D. Kuck, *SynLett* **1993**, 344–347. – [1b] 12. Communication: D. Kuck, M. Seifert, *Chem. Ber.* **1992**, *125*, 1461–1469.

[2] W. Baker, J. F. W. McOmie, S. D. Parfitt, D. A. M. Watkins, *J. Chem. Soc.* **1957**, 4026–4037.

[3] [3a] Stability of **1** relative to the C_2-symmetrical [2,1-*a*] isomer, see, for example: M. Randić, *J. Am. Chem. Soc.* **1979**, *99*, 444–450. – [3b] Syntheses of the [2,1-*a*] isomer of **1**: C. C. Chuen, S. W. Fenton, *J. Org. Chem.* **1958**, *23*, 1538–1539, and previous reports.

[4] A particularly short and efficient synthesis of **2** has been published recently: D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449–1460. In that paper, the synthesis of the title compound **4**, from 2-benzhydryl-1,3-indandiol (11% yield) is also described.

[5] [5a] W. H. Laarhoven, F. A. T. Lijten, J. M. M. Smiths, *J. Org. Chem.* **1985**, *50*, 3208–3209. – [5b] J. M. M. Smits, J. H. Noordik, P. T. Beurskens, W. H. Laarhoven, F. A. T. Lijten, *J. Cryst. Spectrosc. Res.* **1986**, *16*, 23–29. – [5c] E. Ciganek, *J. Am. Chem. Soc.* **1966**, *88*, 2882–2883.

[6] D. Kuck in *Quasicrystals, Networks, and Molecules of Fivefold Symmetry* (Ed.: I. Hargittai), VCH Publishers, New York, **1990**, Chapter 19.

[7] Frequently, the positions of tribenzotriquinacenes are numbered according to those of the parent hydrocarbon, triquinacene. The IUPAC nomenclature of **4** is 4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene with the central carbon atom being defined as C-12d, for example.

[8] Short communications: [8a] D. Kuck, *Angew. Chem.* **1984**, *96*, 515–516; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 508–509. – [8b] D. Kuck, H. Bögge, *J. Am. Chem. Soc.* **1986**, *108*, 8107–8109.

[9] The syntheses of several higher centropolyindans (including **4**) by twofold cyclodehydration of 1,3-indandiols is reported in detail in ref.[4] and in: [9a] D. Kuck, *Chem. Ber.*, in press. – [9b] See also M. Seifert, Ph. D. Thesis, University of Bielefeld, **1991**.

[10] D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626–628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595–597.

[11] P. Gund, T. M. Gund, *J. Am. Chem. Soc.* **1981**, *103*, 4458–4465.

[12] P. Pfeiffer, H. L. de Waal, *Liebigs Ann. Chem.* **1935**, *520*, 185–200.

[13] [13a] J. Sharvit, A. Mandelbaum, *Org. Mass Spectrom.* **1976**, *11*, 488–498. – [13b] A. Mandelbaum in *Stereochemistry* (Ed.: H. B. Kagan), vol. 1, Thieme, Stuttgart, **1977**, p. 137ff.

[14] [14a] H.-F. Grützmacher, R. Asche, *Chem. Ber.* **1975**, *108*, 2080–2096. – [14b] J. Espinosa Gonzalez, H.-F. Grützmacher, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 181–194.

[15] D. Kuck, U. Filges, *Org. Mass Spectrom.* **1988**, *23*, 643–653.

[16] D. Kuck, *Adv. Mass Spectrom.* **1986**, *10*, 773–774.

[17] Hindered rotation of phenyl groups oriented to the concave side of a diindan skeleton have been observed (cf. ref.[1b]).

[18] A. Gaudemer in *Stereochemistry* (Ed.: H. B. Kagan), vol. 1, Thieme, Stuttgart, **1977**, p. 44ff.

[19] For coupling constants of stereoisomeric 9,10-disubstituted diindans of type **2**, see: [19a] K. E. Richards, R. W. Tillman, G. J. Wright, *Aust. J. Chem.* **1975**, *28*, 1289–1300. – [19b] S. S. Hixson, D. W. Garrett, *J. Am. Chem. Soc.* **1974**, *96*, 4872–4879. – [19c] S. J. Cristol, W. Y. Lim, A. R. Dahl, *J. Am. Chem. Soc.* **1970**, *92*, 4013–4017.

[20] For a discussion of the conformation and ^{1}H-^{1}H spin coupling of 4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene, a C_2-symmetrical isomer of **2**, and its $Cr(CO)_3$ complexes, see: A. Ceccon, A. Gambaro, F. Manoli, A. Venzo, P. Ganis, D. Kuck, G. Valle, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1111–1117.

[21] Baker et al.[2] only stated that 60% of the starting material **8** is recovered.

[22] D. Kuck, E. Neumann, unpublished results.

[23] J. Espinosa Gonzales, D. Kuck, unpublished results.

[24] [24a] B. Schaldach, H.-F. Grützmacher, *Org. Mass Spectrom.* **1980**, *15*, 175–181. – [24b] B. Schaldach, H.-F. Grützmacher, *Int. J. Mass Spectrom. Ion Phys.* **1979**, *31*, 257–270.

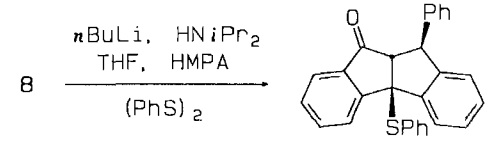
[25] The separation and identification of **15** and **16** will be further pursued in this laboratory.

[26] [26a] E. Mincione, G. Ortaggi, A. Sirna, *Synthesis* **1977**, 773–774. – [26b] G. Mehta, K. R. Reddy, R. Gleiter, S. Lalitha, J. Chandrasekhar, *J. Org. Chem.* **1991**, *56*, 7048–7055.

[27] [27a] H. J. Reich, J. M. Renga, I. L. Reich, *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447. – [27b] H. J. Reich, *Acc. Chem. Res.* **1979**, *12*, 22–30.

[28] [28a] B. M. Trost, T. N. Salzmann, K. Hiroi, *J. Am. Chem. Soc.* **1976**, *98*, 4887–4902. – [28b] B. M. Trost, *Chem. Rev.* **1978**, *78*, 363–382.

[29] Phenylsulfenylation of **8** in the presence of hexamethylphosphoramide (HMPT, cf. ref.[28]) leads to the formation of the regioisomer **34**, bearing the phenylthio group at the bridgehead position C-4b.



34

Oil; ^{1}H NMR (300 MHz): δ = 8.04 (d, ^3J = 7.4 Hz, 1H), 7.81 (d, ^3J = 8.0 Hz, 1H), 7.65 (td, ^3J = 7.5, ^4J = 1.3 Hz, 1H), 7.56 (dd, ^3J = 7.2, ^4J = 0.9 Hz, 1H), 7.33 (d, ^3J = 6.9 Hz, 1H), 7.28 (d, ^3J = 7.3 Hz, 1H), 7.11–7.27 (m, 5H), 6.92–7.04 (m, 6H), 6.82 (d, ^3J = 7.7 Hz, 1H), 4.44 (d, ^3J = 4.4 Hz, $\nu_{1/2}$ ≈ 3 Hz, 1H, 10-H), 3.52 (d, ^3J = 4.4 Hz, $\nu_{1/2}$ < 0.5 Hz, 1H, 9a-H). – ^{13}C NMR (75 MHz): δ = 204.7 (s, C=O), 156.4 (s), 144.5 (s), 144.3 (s), 143.3 (s), 136.1 (d), 135.7 (d), 135.2 (s), 131.9 (s), 129.22 (d), 129.13 (d), 128.87 (d), 128.61 (d), 128.25 (d), 128.10 (d), 126.63 (d), 126.2 (d), 125.5 (d), 124.7 (d), 124.0 (d), 67.69 (d), 67.42 (s, C-4b), 52.6 (d). – MS, *m/z* (%): 404 (1.5) [M$^{\bullet+}$], 295 (100) [M$^{\bullet+}$ – PhS], 294 (6), 265 (15), 263 (7), 252 (5), 239 (3), 217 (18), 189 (8), 165 (4), 109 (17).

[30] Attempts to epimerize **27** to **26** by using S_N1 or S_N2 pathways were unsuccessful: From treatment of **27** with *p*-toluenesulfonic acid in toluene or with *p*-toluenesulfonyl chloride in pyridine the starting material was recovered unchanged.

[31] The complete IR spectrum of **4** has been published: *Sadtler Standard Spectra,* Sadtler Research Laboratories, Philadelphia, PE, **1991**, No. 79908 K.

[32] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, Thieme, Stuttgart, **1984**, Chapter 2.

[33] [33a] V. J. Traynelis, W. J. Hergenrother, J. R. Livingston, J. A. Valicenti, *J. Org. Chem.* **1962**, *27*, 2377–2383. – [33b] V. J. Traynelis, W. J. Hergenrother, H. T. Hanson, J. A. Valicenti, *J. Org. Chem.* **1964**, *29*, 123–129. – [33c] R. Askani in *Methoden der Organischen Chemie (Houben-Weyl), 4. ed.*, **1952–1991**, vol. 5/1b, p. 83–104.

[34] D. Kuck, *Z. Naturforsch., Teil B*, **1984**, *39*, 369–374.

[35] In our recent paper[4] we erronously assigned the diindene **32** as the main product of dehydration of 2-benzhydryl-1,3-indandiol. In fact, the product assigned structure **9** there (Scheme 8) is identical with the olefin **30** of this work.

[36] E. Vogel, *Chem. Ber.* **1952**, *85*, 25–29.

[37] T. Matsuzaki, *Acta Cryst., Sect. B*, **1974**, *30*, 2060–2061.

[38] W. M. Harms, E. J. Eisenbaum, *Org. Prep. Proced. Int.* **1971**, *3*, 239–242.

[232/93]