for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.69; H, 7.28.

The second component contained 46 mg (23%) of **13**. The third component contained 72 mg (36%) of diastereomers **12a** and **12b**.

Triplet-Sensitized Irradiation of 1-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)-3-phenylindene (7). A solution containing 300 mg of indene **7** and 55 mg of thioxanthen-9-one in 250 mL of benzene was irradiated through a Uranium filter sleeve for 30 min. The solvent was removed under reduced pressure, and the resulting residue was passed through a small silica gel column using hexane as the eluent. The major fraction (80%) was a clear oil whose structure was assigned as **2,2a,7,7a-tetrahydro-2,2a-dimethyl-1,7,8-triphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (22)**: NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 3 H), 1.70 (s, 3 H), 3.82 (s, 1 H), and 6.5–7.6 (m, 19 H); IR (neat) 1590, 1495, 1370, 1165, 1065, 740, and 705 cm^{-1}; UV (cyclohexane) 273 nm (ϵ = 5500) and 277 (ϵ = 17400); *m/e* 410 (M^+, base), 396, 395, 380, 319, 318, 317, 303, 302, 232, 217, 216, 215, 205, 151 and 91. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.38; H, 6.17.

The following compounds were prepared by triplet sensitized irradiations as described above for **7** with the indene, sensitizer, solvent and irradiation times specified. Photoproducts **24–26** were purified by medium-pressure silica gel chromatography with hexane.

2,2a,7,7a-Tetrahydro-2,7-dimethyl-1,2a,8-triphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (23). Indene **8** (240 mg) and thioxanthen-9-one (60 mg) in benzene (250 mL) was irradiated for 15 min to give **23** (88%): NMR ($CDCl_3$, 100 MHz) δ 1.43 (s, 6 H), 3.07 (s, 1 H), 6.40–6.65 (m, 2 H), and 6.9–7.5 (m, 17 H): IR (neat) 1595, 1445, 1060, 780, 715, and 695 cm^{-1}; UV (cyclohexane) 272 nm (ϵ = 3900) and 216 (ϵ = 15900); *m/e* 410 (M^+, base), 396, 380, 317, 302, 239, 232, 217, 202, 191, 178, 165, 151, 115, 91, and 77. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.54; H, 6.13.

2-Ethyl-2a,7-dimethyl-1,8-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (24). Indene **11** (126 mg) and thioxanthen-9-one (23 mg) in benzene (250 mL) was irradiated for 35 min to give 91 mg (72%) of **24**: IR (neat) 1600, 1520, 1385, 1075, 750, 725, and 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.07 (t, 3 H, *J* = 8 Hz), 1.43 (s, 6 H), 1.97 (q, 2 H, *J* = 8 Hz), 3.07 (s, 1 H), and 6.37–7.43 (m, 14 H); UV (95% ethanol) 227 nm (ϵ = 22700); *m/e* 362 (M^+), 360, 347, 332, and 319. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.61; H, 7.05.

2-Ethyl-7,8-dimethyl-1,2a-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (25). Indene **14** (297 mg) and thioxanthen-9-one (53 mg) in benzene (500 mL) was irradiated to give 287 mg (97%) of **25**: IR (KBr) 1610, 1500, 1390, 1075, 755, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.80 (t, 3 H, *J* = 8.0 MHz), 1.43 (s, 3 H), 1.58 (s, 3 H), 2.30 (sex, 2 H, *J* = 8.0 Hz), 2.97 (s, 1 H), and 6.38–7.47 (m, 14 H); UV (95% ethanol) 272 (ϵ = 6260) and 228 nm (ϵ = 24870); *m/e* 362 (M^+), 333, 255, 215, 205, 184, and 178. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.50; H, 7.28.

2-Ethyl-1,7-dimethyl-1a,8-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (26). Indene **13** (110 mg) and thioxanthen-9-one (20 mg) in benzene (200 mL) was irradiated to give 102 mg (93%) of **26**: IR (KBr) 1600, 1390, 1075, 910, 770, 755, and 705 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.96 (t, 3 H, *J* = 8 Hz), 1.43 (s, 3 H), 1.82 (s, 3 H), 1.83 (q, 2 H, *J* = 8 Hz), 2.62 (s, 1 H), and 6.20–7.46 (m, 14 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 9.9, 15.5, 16.9, 23.9, 45.5, 47.7, 48.6, 60.4, 68.1, and 120.1–150.2; UV (95% ethanol) 272 nm (ϵ = 10950); *m/e* 362 (M^+), 347, 334, and 318. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.72; H, 7.27.

Acknowledgment. This work was supported by the National Science Foundation. Use of the high-field NMR spectrometers used in these studies was made possible through equipment grants from the National Science Foundation and the National Institutes of Health.

Synthesis and Reactions of 9,10,11-Triptindantrione and Some Other Functionalized Tribenzo[3.3.3]propellanes (9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]indenes)[1]

Bernd Paisdor and Dietmar Kuck*

Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-4800 Bielefeld 1, Federal Republic of Germany

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A new and efficient route to the tribenzo[3.3.3]propellane **1** (triptindan) and to some interesting derivatives such as 9-triptindanone (**13**) and 9,10,11-triptindantrione (**3**) has been developed. The propellane framework of **13** is accessible from 1,3-indandione in only two steps. Triketone **3**, a versatile substrate with formal C_{3v} molecular symmetry, is obtained from **13** in two further steps. First examples are presented for reactions of **3** leading to more complex benzoannelated centropolyquinanes (centropolyindans).

Mutual annelation of several indan units along the bonds of the five-membered rings leads to centropolyquinanes[2] bearing several benzo nuclei at the molecular periphery. This new group of centropolycyclic aromatic hydrocarbons ("centropolyindans")[3] thus combine the rich three-dimensional structural variety of polyquinanes[4] with the well-known chemical features of arenes. The synthetic access to higher centropolyindans with up to six centrically fused indan units has been reported recently.[5]

(1) Benzoannelated Centropolyquinanes. 8. Parts 6 and 7: refs 5d and 3, respectively. Presented, in part, at the 200th ACS National Meeting, Washington, DC, August 26–31, 1990; American Chemical Society: Washington, DC, 1990; ORGN 316.

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

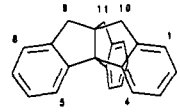
(3) Kuck, D. In *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*; Hargittai, I., Ed.; VCH Publishers: New York, 1990; Chapter 19.

(4) (a) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry, Synthesis and Reactions*; Springer-Verlag: Berlin, 1987. (b) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1–160. (c) Paquette, L. A. *Ibid.* **1979**, *79*, 41–165.

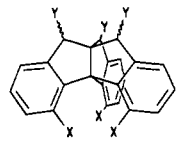
(5) (a) Kuck; D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 508. (b) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* **1986**, *108*, 8107. (c) Kuck, D.; Schuster, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1192. (d) Kuck, D.; Schuster, A.; Ohlhorst, B.; Sinnwell, V.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 595.

0022-3263/91/1956-4753$02.50/0

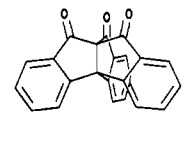
The first centrotriindan, triptindan, 1, was synthesized by Thompson more than two decades ago.[6-9] The propellane-type carbon framework of 1[10] with formal C_{3v} molecular symmetry bears two regions of particular interest, as illustrated by formula 2. Following Thompson's synthetic strategy,[6] we recently synthesized triptindans with three sterically interacting substituents in the molecular cavity of 2 (X = Me, OMe, OH; Y = H).[11]



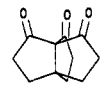
1



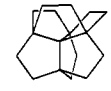
2



3



4



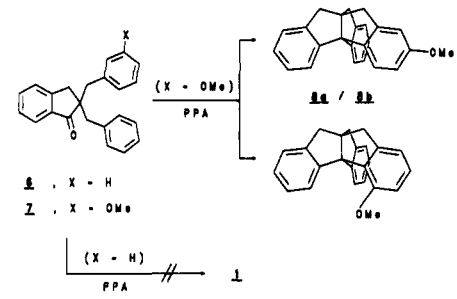
5

In the present paper, we wish to report a new, extremely efficient, three-step synthesis of the parent triptindan 1, starting from 1,3-indandione (11). The new approach offers a ready access to triptindans bearing functional groups of the "top" of the carbon framework of 1, i.e., in positions 9, 10, and 11 (2, X = H; Y ≠ H). As the most remarkable derivative, 9,10,11-triptindantrione (3) has been prepared. Some reactions of these new triptindans have been studied in analogy to those of the corresponding nonbenzoannelated [3.3.3]propellanes, e.g., Conia's triketone 4,[12] which were directed toward the synthesis of the elusive centrohexaquinane 5.[13,14]

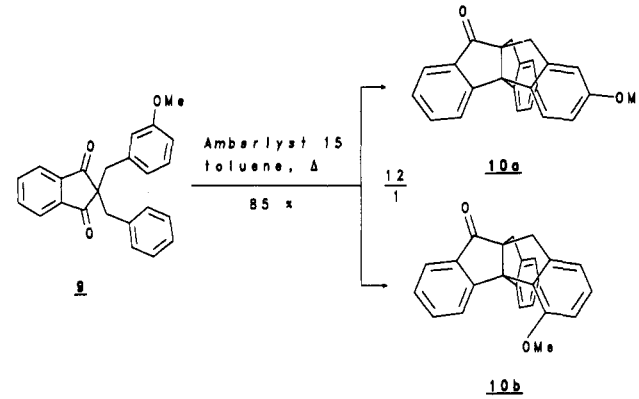
Results and Discussion

New Synthesis of Triptindan. The key step of Thompson's triptindan synthesis is the acid-catalyzed cyclodehydration of substituted 2,2-dibenzyl-1-indanone 7 in polyphosphoric acid (PPA), which leads to a 7:1 mixture of the methoxytriptindans 8a and 8b in excellent yield (97%). At least one *m*-methoxy substituent is required to achieve the cyclization; the unsubstituted ketone 6 does not undergo this reaction under a variety of conditions, including treatment with PPA (Scheme I). Therefore, besides the classical three-step synthesis of 7 (and 6), another three steps are necessary to convert the major triptindan isomer 8a to the parent hydrocarbon 1.[6b]

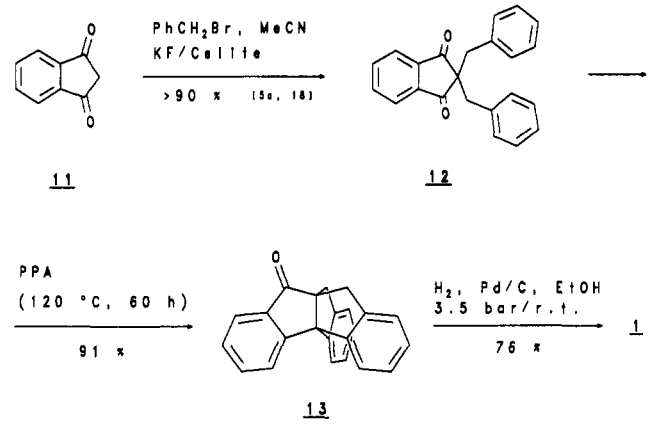
Scheme I



Scheme II



Scheme III



The double cyclization strategy (cf. 7 → 8) proved very useful to prepare other substitued triptindans, in particular sterically crowded derivatives 2.[11,15,16] Controlled functionalization of the methylene groups of 1 or 8, however, aimed to extend to the polycyclic framework, appeared to be difficult.

In order to obtain 9-functionalized triptindans, we now successfully transposed Thompson's strategy to the corresponding 2,2-dibenzyl-1,3-indan*diones* 9 and 12 (Schemes II and III). In fact, the *m*-methoxy derivative 9 is cyclodehydrated to the corresponding 9-triptindanones 10a and 10b. The reaction takes place not only in PPA but also with the relatively mild ion exchange resin Amberlyst 15 (A 15) in boiling toluene.[17] As the latter reaction conditions apply also to the cyclodehydration of 7 → 8a/8b, the mono- and diketones 7 and 9 appear to exhibit

(6) (a) Thompson, H. W. *Tetrahedron Lett.* **1966**, 6489. (b) Thompson, H. W. *J. Org. Chem.* **1968**, *33*, 621.

(7) As Professor Thompson communicated to us, the original name of 1 coined by him was "triptindane", with reference to the "ane" nomenclature. This journal turned it to "triptindan". In fact, we also prefer the ending "an" used correctly for all kinds of indans (and furans, etc.). It may be noted as a curiosity, however, that there are indeed "indanes" in chemistry (InH_3 and its derivatives).

(8) In analogy to Gund and Gund's suggestions,[2] 1 and its derivatives have be termed *monofuso*-centrotriindans,[3] referring to the fusion of three indan units along one common C–C bond.

(9) Previous to our work (cf. refs 3 and 5), a *difuso*-centrotriindan was synthesized: Ten Hoeve, W.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2930.

(10) Ginsburg, D. *Propellanes, Structures and Reactions*; Verlag Chemie: Weinheim, 1975.

(11) (a) Kuck, D.; Paisdor, B.; Grützmacher, H.-F. *Chem. Ber.* **1987**, *120*, 589. (b) Paisdor, B.; Grützmacher, H.-F.; Kuck, D. *Ibid.* **1988**, *121*, 1307.

(12) (a) Prange, T.; Drouin, J.; Leyendecker, F.; Conia, J.-M. *J. Chem. Soc., Chem. Commun.* **1977**, 430. (b) Gleiter, R.; Litterst, E.; Drouin, J. *Chem. Ber.* **1988**, *121*, 923.

(13) (a) Simmons, H. E., III; Maggio, J. E. *Tetrahedron Lett.* **1981**, *22*, 287. (b) Simmons, H. E., III. PhD Thesis, Harvard University, 1980.

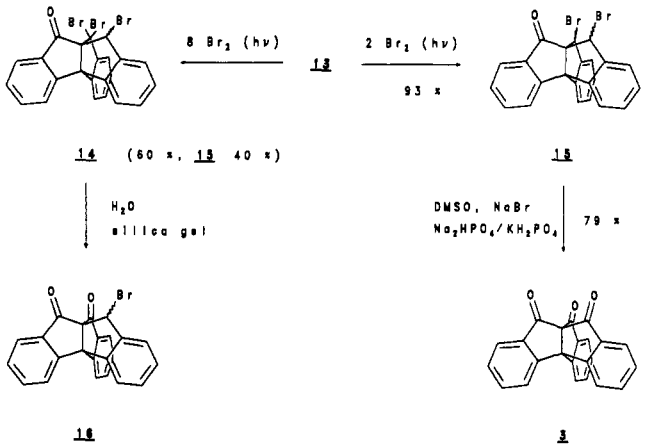
(14) (a) Paquette, L. A.; Vazeux, M. *Tetrahedron Lett.* **1981**, *22*, 291. (b) Paquette, L. A.; Williams, R. V.; Vazeux, M.; Browne, A. R. *J. Org. Chem.* **1984**, *49*, 2194.

(15) Paisdor, B. Doctoral Thesis, Universität Bielefeld, 1989.

(16) Kuck, D.; Paisdor, B.; Wacker, D. Unpublished results.

(17) (a) Harms, W. M.; Eisenbraun, E. J. *Org. Prep. Proc. Int.* **1971**, 239. (b) Harms, W. M.; Eisenbraun, E. J. *Ibid.* **1972**, *67*.

Scheme IV



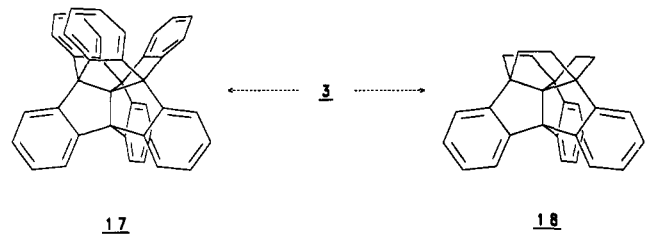
similar reactivities with respect to cyclodehydration.

According to the results collected so far, unsubstituted 2,2-dibenzyl-1,3-indandione **12** seemed not suitable for constructing the triptindan framework. Notwithstanding, **12** appeared to be an attractive starting material for this purpose because of its ready one-step synthesis from 1,3-indandione **11** in excellent yield (Scheme III).[5a,18] In fact, **12** does not cyclize in boiling toluene or xylene with A 15 or phosphoric acid as catalysts. Under these conditions, the activation by a *m*-methoxy group is required (cf. **9** → **10**). By contrast, cyclodehydration of **12** is achieved by using PPA at only (!) 120 °C, affording 9-triptindanone **13** in 91% isolated yield. Subsequent hydrogenolysis of **13** gives the parent hydrocarbon **1** in (nonoptimized) 76% yield. Thus, **1** can be synthesized in only three steps from 1,3-indandione (**11**) in at least 66% overall yield.

It is interesting to speculate on the finding that the 1,3-indandione **12** undergoes cyclization to the triptindan skeleton whereas the 1-indanone **6** does not. Thompson[6b] attributed the latter finding to the lack of electronic activation of the benzyl group to be reacted in the first cyclization step, as well as to the decreased solubility of **6** in PPA, as compared to the methoxy derivative **7**. The activating effect of methoxy (and hydroxy) substituents positioned para to the site of electrophilic attack is a well-known, general phenomenon in cyclodehydration reactions.[19,20] By contrast, efficient cyclization of ketones with *unsubstituted* or deactivated arene moieties has been performed rarely.[21]

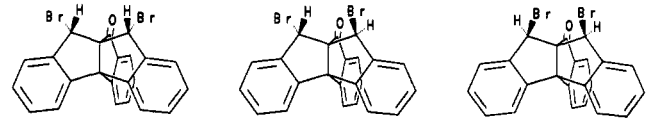
9,10,11-Trifunctionalized Triptindans. 9-Triptindanone **13** has been further functionalized by bromination to give the bromo ketones **14** and **15**. The latter ketone can be readily oxidized to 9,10,11-triptindantrione **3** by Kornblum oxidation[23] (Scheme IV). This triketone, a tribenzo analogue of **4**, is not accessible by direct oxidation using, for example, Cr^{VI} or Mn^{IV}.[15] The two-step sequence displayed in Scheme IV, however, affords the triketone **3** in 73% overall yield from **13**.

Scheme V



Use of excess bromine (molar ratio $[Br_2]$:[13] = 8:1) leads to the formation of 60% tribromo ketone **14** along with 40% of dibromo ketone **15**. The large substituents in **14** give rise to considerable steric crowding at the top of the molecule.[15] It may be due to this reason that **14** rapidly hydrolyzes during elution from a silica gel column with chloroform giving the bromodiketone **16** (Scheme IV).

In contrast, use of 2 equiv of bromine gives the dibromo ketone **15** as a stable compound in excellent yield (93%). Inspection of the 300-MHz ^1H NMR spectrum suggests the formation of a single, unsymmetrical (C_1) stereoisomer, excluding not only the heavily crowded *proximal* isomer (**15p**) but, most probably, also the *distal* one (**15d**). According to force-field (MMPMI) calculations,[15,24] the latter should be only slightly ($\simeq$1 kcal·mol^{-1}) more stable than the *medial* isomer **15m**. Partial torsion along the propellane axis of **15m** should relieve some steric strain, possibly leading to an equilibrium of two rotamers.[11b] The lack of molecular symmetry of **15m** is reflected by two 1:1 singlets at δ 6.22 and 6.24 (see Experimental Section).

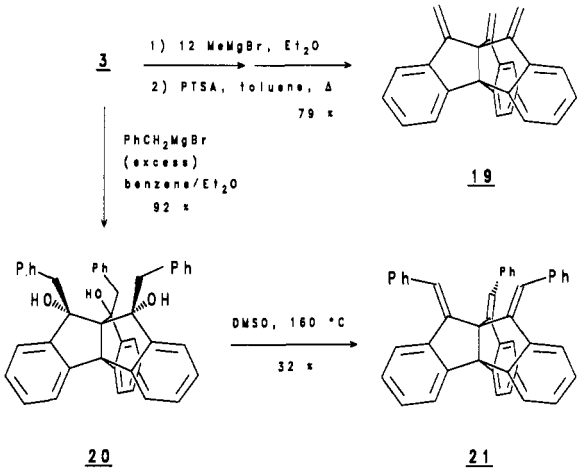


The identity of 9,10,11-triptindantrione **3** is confirmed unambigiously by its spectroscopic properties, in particular by the simple NMR spectra. It is a crystalline, colorless solid with a mp > 360 °C and of extremely low solubility in common organic solvents ($\simeq$7 g/L in boiling THF). Nevertheless, suspensions of **3** can be handled without complications in preparations using this triketone as a key substrate to modify or enlarge the triptindan framework. Some of these experiments will be described in the following paragraphs.

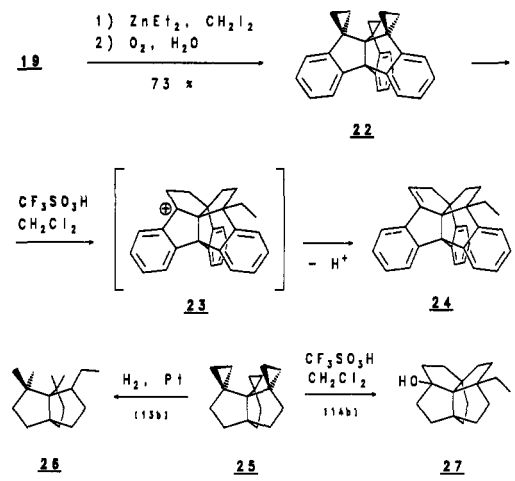
First Attempts toward Tribenzocentrohexaquinanes. It appears tempting to use triptindantrione **3** as a versatile starting material to construct chiral compounds with C_3 or C_{3v} molecular symmetry. In the present work, we restrict ourselves to the discussion of experiments directed to triptindans bearing various functional groups or rings at the top of the molecule. As shown separately,[1,25] **3** represents the substrate for a novel, extremely short, and efficient synthesis of centrohexaindan **17**.[5c] Beyond that, the triketone **3** could also serve as a starting point for the synthesis of centropolyquinanes with *lower* degree of benzoannelation, e.g., the tribenzocentrohexaquinane **18** (Scheme V). We tried to synthesize **18** in close analogy to Simmons' and Paquette's attempts to prepare the

(18) Kuck, D. Manuscript in preparation.
(19) Bradsher, C. K. *Chem. Rev.* **1946**, *38*, 447–449.
(20) Angle, S. R.; Louie, M. S. 200th ACS National Meeting, Washington, DC, August 26–31, 1990; American Chemical Society: Washington, DC, 1990; ORGN 024.
(21) There are in fact additional hints pointing to the importance of solubility of the substrate ketone in PPA (cf. ref 22), and the diketone **12** appears indeed to be more soluble in PPA than **6**. On the other hand, **12** may as well be activated electronically. The stabilized hydroxyindanyl ions formed upon protonation of 1-indanones require the presence of electron-rich benzyl groups to undergo cyclization (e.g., **7** vs **6**). In the case of 1,3-indan*dione* **12**, however, the lack of electronic activation of the benzyl group is compensated by a *destabilization* of the hydroxyindanyl ion due to the additional keto group.
(22) (a) Popp, F. D.; McEwen, W. E. *Chem. Rev.* **1958**, *58*, 321–401. (b) Uhlig, F.; Snyder, H. R. *Adv. Org. Chem.* **1960**, *1*, 35–81.
(23) (a) Kornblum, N.; James, W. J.; Anderson, G. J. *J. Am. Chem. Soc.* **1959**, *81*, 4113–4114. (b) Epstein, W. W.; Sweat, F. W. *Chem. Rev.* **1967**, *67*, 247–260. (c) Durst, T. *Adv. Org. Chem.* **1969**, *6*, 285–388. (d) Babler, J. H.; Coghlan, M. L.; Feng, M.; Fries, P. *J. Org. Chem.* **1979**, *44*, 1716–1717.
(24) Gajewski, J. J.; Gilbert, K. E. *QCPE*, Indiana, 1986.
(25) Kuck, D.; Bögge, H.; Müller, A.; Paisdor, B.; Schuster, A. To be published.

Scheme VI



Scheme VII

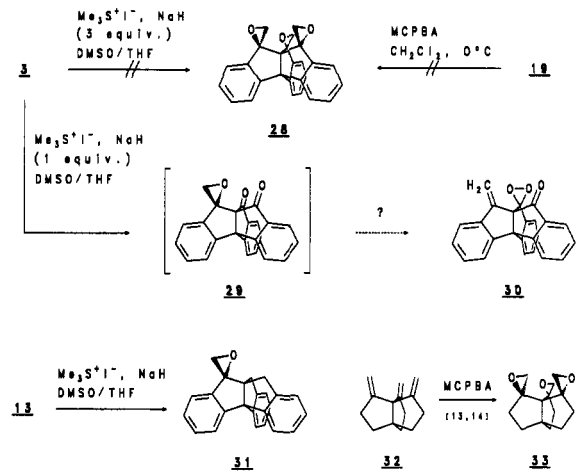


parent hexaquinane **5**. With regard to the conformational flexibility of **1**[11b] and the rigidity of **17** and other centropolyindans containing triquinacene subunits,[3,26-28] **18** should exhibit interesting structural features and conformational dynamics.

Reaction of **3** (Scheme VI) with excess methyl Grignard in diethyl ether followed by acid-catalyzed 3-fold dehydration during the workup procedure furnishes 9,10,11-trimethylenetriptindan **19** in 80% yield.[29] Similarly, **3** gives the corresponding tribenzylidene analogue **21**, albeit in relatively low yield, by reaction with large excess of benzyl Grignard in benzene. The crude triol **20** (92%) is dehydrated in DMSO at 160 °C to give **21** as the a single stereoisomer and the only identifiable product. The stereochemistry of **21** as a 3-fold *cis*-stilbene derivative follows from the simplicity of the ^1H and ^{13}C NMR spectra, which again reflect a C_3-symmetrical structure. The corresponding 3-fold *trans*-stilbene can be excluded for sterical reasons. The cis stereochemistry of **21** suggests the possibility to generate 3-fold condensed phenanthrenes by oxidative photocyclization. Addition of aryl Grignard and related reagents to **3** are described elsewhere.[25]

Threefold cyclopropanation of **19** (Scheme VII), in analogy to the procedure used for the parent [3.3.3]propellatriene **32** (Scheme VIII),[13,14,30a] gives the triptindan-9,10,11-trispirocyclopropane **22** in 73% isolated yield. A 15–20-fold excess of the carbenoid reagent has to be used to suppress incomplete cyclopropanation. The C_3 molecular symmetry of **22** is reflected by the ^1H NMR resonances of the aromatic rings, whereas the signals of the cyclopropane rings are not completely resolved. This is attributed to the reduced flexibility of this propellane and the "in/out" inversion of the "crown" moiety.[30a,31]

Scheme VIII



Some experiments were performed to compare the reactivity of **22** to that of the corresponding nonbenzoannelated trispirane **25**.[13,14,30b] Simmons[13b] subjected **25** to hydrogenolysis (Pt/acetic acid, 1 bar/rt) and found cleavage of the cyclopropane rings to give the corresponding tetramethylethylpropellane **26**. By contrast, **22** is recovered essentially unchanged after even more drastic treatment (e.g., 5 bar/50 °C); neither hydrogenolysis nor isomerization products (e.g., **18**) were found. The inertness of **22** as well as the unusual course of cyclopropane ring hydrogenolysis found for **25**[13b] may reflect the severe steric crowding of the (cyclo)alkyl groups at the top of the [3.3.3]propellane skeleton.

Paquette et al.[14b] reported the acid-catalyzed rearrangement of **25** to the centropentaquinane alcohol **27** as the only well-defined reaction of this propellane leading to higher polyquinanes. By adopting Paquette's experimental procedure (trifluoromethanesulfonic acid as the catalyst) we find, in close analogy, that **22** is rearranged to the tribenzocentropentaquinene **24**. Obviously, initial protonolysis of a cyclopropane ring and two subsequent 1,3-C shifts lead to the benzylic carbenium ion **23**, which gives **24** either by direct deprotonation or by elimination of the corresponding triflate. The formation of **24** is strongly suggested on the basis of its ^1H NMR spectrum, which shows, similar to the spectrum of alcohol **27**,[14b] the presence of an ethyl group (triplet at δ 0.68). Moreover, the allylic group of the cyclopentene ring is clearly indicated by an ABX spin system caused by the olefinic proton (δ 5.74) and the methylene protons (δ 3.21 and 3.00). As may be expected for this strained, bridgehead styrene, **24**

(26) Ermer, O. *Aspekte von Kraftfeldrechnungen*; Wolfgang-Baur-Verlag: München, 1981; Chapter 4.6.3.
(27) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington DC, 1982; Chapter 4.
(28) Osawa, E. *J. Am. Chem. Soc.* **1979**, *101*, 5523–5529.
(29) Reaction of **3** with 2.6 equiv of the Grignard reagent gives, after isolation by MPLC ($CHCl_3$), 10,11-bis(methylene)triptindan-9-one, mp 265 °C; δ ($CDCl_3$) for $H^{methylene}$ 5.89 and 5.77 (s; 2 H each).
(30) (a) Maggio, J. E.; Simmons, H. E., III; *J. Am. Chem. Soc.* **1981**, *103*, 1579–1581. (b) Benner, S. A.; Maggio, J. E.; Simmons, H. E., III: *J. Am. Chem. Soc.* **1981**, *103*, 1581–1582.
(31) The dynamic behavior of trispirane **25** was studied by Simmons et al.[13b,30a] The tribenzo analogue **22**, likewise, exhibits temperature-dependent ^1H NMR spectra (300 MHz, DMSO-d_6), reflecting the in/out inversion of the three cyclopropane rings. Even at 100 °C, however, the *ABCD* spin systems do not collapse to the pattern (*AA'BB'*) expected for rapidly interconverting rotamers. The coalescence temperature should be considerably higher. Hence, the free activation energy for the rotation along the propellane bond of **22** should by higher than that of **25** ($\simeq$62 kJ mol^{-1};[30a] see also refs 11b and 15).

readily decomposes after standing for some days. Other isotriquinacenes have been described by several groups and were found to be relatively unstable with respect to the corresponding triquinacenes.[32-34] In the present work, no attempt has been made to shift the double bond in **24** away from the bridgehead position.

Attempts to synthesize the trisepoxide **28** (Scheme VIII) from either triketone **3** or triene **19** proved unsuccessful. Simmons et al.[13] and Paquette et al.[14] converted the triene **32** to the trisepoxide **33** by using *m*-chloroperbenzoic acid (MPCBA) at low temperatures. Unfortunately, under the same as well as under modified experimental conditions, the triptindan analogue **19** gives a multicomponent mixture of unidentified products. We believe that, similar to the protonolysis of **22** to **24**, the presence of the benzo rings leads to benzylic labilization, which is possibly enhanced by increased steric hindrance due to the relatively unflexible five-membered rings. Similar arguments may hold for our unsuccessful attempts to obtain **28** by 3-fold methenylation of **3**. The simpler spiro oxirane **31** can in fact be obtained by methenylation of 9-triptindanone **13** with dimethylsulfonium methylide.[35] **31** is stable as a solid but rapidly decomposes in solutions at room temperature.[15] Treatment of trione **3** with 3 equiv of the sulfonium ylide gives rise to the formation of a variety of decomposition products. Use of only 1 mol of the reagent yields an extremely labile monomethenylation product, which is certainly *not* the expected diketo oxirane **29** but rather an unconventional rearrangement product, to which we tentatively assigned the structure of the ketodioxirane **30** (see Experimental Section).[15,36,37]

These results demonstrate that, in contrast to the general experience, benzoannelation may complicate the chemistry of (centro)polyquinanes by increasing the reactivity of electrophilic centers and the steric strain in crowded molecular arrangements. More detailed studies will be necessary to synthesize further centropolyquinanes with a *low* degree of benzoannelation and other partially benzoannelated centrohexaquinanes such as **18**.[38]

Concluding Remarks

A particularly short and efficient access to the molecular framework of triptindan (**1**) has been developed. Several functionalized triptindans have been presented here, among which triptindan-9,10,11-trione (**3**) is certainly the most interesting building block for the synthesis of a large variety of complex benzoannelated centropolyquinanes. **3**, representing a member of the very small family of *triacylmethane* derivatives, undergoes 3-fold addition with nucleophiles without notable fragmentation. Beyond that, because of its C_{3v} symmetrical skeleton, triptindantrione could serve as a basis for the preparation of novel *chiral* propellane-type substrates with extended arene periphery.

Experimental Section

General Methods. Most of the standard analytical techniques were used as stated in ref 11. Melting points are uncorrected: Büchi 512, MPLC LiChroprep Si 60, 40–60 μm (Merck), Matrex LC 60 Å, 20–45 μm and 35–70 μm (Grace). Analytical HPLC was performed on a column with Lichrosorb Si 100, 5 μm (Knauer). Thin-layer chromatography: Kieselgel 60 on Al foil (Merck 60 F 254). HPTLC: plates RP-18 (Merck RP-18 F 254 S).

2-(3-Methoxybenzyl)-2-benzylindan-1,3-dione (9). (9). This ketone has been prepared from 2-(3-methoxybenzylidene)-indan-1,3-dione (**37**) via 2-(3-methoxybenzyl)indan-1,3-dione (**38**)[39] by reduction with $NaBH_4$ in pyridine.[40] The procedure is given in the following text.

A suspension of 39.6 g (150 mmol) of **37** in 115 mL of dry pyridine is stirred as 6.00 g (159 mmol) of powdered $NaBH_4$ is added, while the temperature of the mixtures rises to 50 °C. The mixture is kept at this temperature for 1 h and then cooled to 0 °C, and aqueous HCl is added until the precipitation of the red, oily product is complete. The oil is separated from the aqueous phase, which is saturated with Na_2SO_4 and extracted with diethyl ether. The combined oil and organic layers are washed with water, dried with Na_2SO_4, and evaporated. Recrystallization of the reddish residue from MeOH gives 25.5 g (64%) of **38** as yellow crystals, mp 49 °C. R_f (EtOAc): 0.64. IR (KBr): 1730, 1695 (C=O) cm^{-1}. ^1H NMR (60 MHz): δ 8.06–7.63 (m; 4 H; 4,5,6,7-H), 7.08 (m; 1 H; 2^5-H), 6.70 (m; 3 H; arom H), 3.67 (s; 3 H; $-OCH_3$), 3.30 (s; 3 H; 2,α-H). MS: *m/z* 266 (100, $M^{\cdot+}$), 267 (19), 248 (16), 165 (10), 133 (10), 121 (60), 108 (22), 105 (13), 104 (44), 91 (19), 79 (25), 77 (28), 76 (28).

A solution of 26.6 g (100 mmol) of **38** in 150 mL of dry acetonitrile is stirred vigorously and heated at 70 °C as 25.7 g (150 mmol) of freshly distilled benzyl bromide is added, followed by 73 g (5 equiv) of KF/Kieselgur (Celite 454, Fluka). The mixture is vigorously stirred at 70 °C for 3 h. After the mixture is cooled to rt the Celite is filtered off and washed twice with 60 mL of dry THF. The solvents are removed, and the viscous residue is recrystallized from MeOH, giving 33.8 g (95%) of **9** as colorless crystals, mp 100 °C (MeOH). R_f (heptane/EtOAc (2:1)): 0.75. IR (KBr): 2920, 2840 (CH), 1730 (C=O), 1255 (CO) cm^{-1}. ^1H NMR (60 MHz): δ 7.80–7.32 (m; 4 H; 4,5,6,7-H), 6.97 (s; 5 H; arom H), 6.53 (m; 4 H; arom H), 3.60 (s; 3 H; $-OCH_3$), 3.22 (s; 4 H; α,α′-H). MS: *m/z* 356 (69 %, $M^{\cdot+}$), 357 (19), 265 (21), 236 (17), 235 (86), 122 (100), 121 (57), 91, (64). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.89; H, 5.66. Found: C, 80.60; H, 5.65.

2- and 4-Methoxy-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]inden-9-one (Mixture of 10a and 10b). A stirred solution of 10.0 g (28.1 mmol) of **9** in 150 mL of dry toluene and 3.0 g Amberlyst 15 (Fluka) are heated to reflux in a Thiele–Pape extractor filled with freshly activated molecular sieves (4 Å). The reaction is completed after 30–40 h, the catalyst is removed, and the solution is filtered over a short column with silica gel by using $CHCl_3$ as the solvent. The crude, crystalline product is further purified by MPLC, giving 8.07 g (85%) of a mixture of isomers **10a** and **10b** (ratio ≃ 1:12 according to ^1H NMR) as almost colorless crystals, melting range 50–75 °C. R_f (hexane/EtOAc (3:1)); 0.45. IR (KBr): 3070, 2930 (CH), 1715 (C=O), 1265, 1250 (CO) cm^{-1}. ^1H NMR (80 MHz): δ 7.95–7.48 (m; 4 H; arom H), 7.45–6.95 (m; 4 H; arom H), 6.85–6.65 (m; 2 H; 1,3,4-[1,2,3]-H), 3.93 (s; 3 H; 2-OCH_3), 3.70 (s; 3 H; 4-OCH_3), *AB* (δ_A 3.59, δ_B 3.21, J_{AB} = −17.2 Hz; 2 H; 10-H), AB (δ_A 3.59, δ_B 3.24, J_{AB} = −17.0 Hz; 2 H; 11-H). MS: *m/z* 338 (100, $M^{\cdot+}$), 339 (27), 121 (12). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.19; H, 5.36. Found: C, 85.20; H, 5.26.

(32) Paquette, L. A.; Kramer, J. D. *J. Org. Chem.* **1984**, *49*, 1445–1446.

(33) (a) Butenschön, H.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2557–2776. (b) Butenschön, H. Doctoral Thesis, University Hamburg, 1983.

(34) (a) Gupta, A. K.; Lannoye, G. S.; Kubiak, G.; Schkeryantz, J.; Wehrli, S., Cook, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 2169–2179. (b) Gupta, A. K.; Cook, J. M. *Tetrahedron Lett.* **1988**, *29*, 2535–2538. (c) Gupta, A. K.; Fu, X.; Snyder, J. P.; Cook, J. M. To be published.

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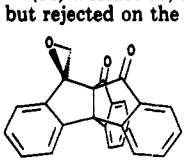
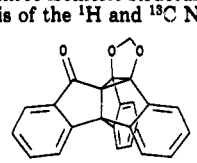
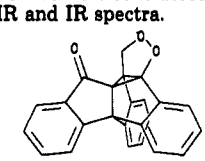
(36) Besides **30**, the three isomeric structures **34–36** were considered but rejected on the basis of the ^1H and ^{13}C NMR and IR spectra.



34



35



36

(37) For reviews on dioxiranes, see: (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187–1201. (b) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 207–211.

(38) **3** readily reacts with 3 equiv of [β-(trimethylsilyl)vinyl]magnesium bromide to give the corresponding triol. However, by no means a 3-fold cyclocondensation to the corresponding tribenzocentrohexaquina*triene* could be achieved.[15]

(39) Okukawa, T.; Suzuki, K.; Sekiya, M. *Chem. Pharm. Bull.* **1974**, *22*, 448–451.

(40) Aren, B. E.; Dauvarte, M. P.; Aren, A. K. *J. Org. Chem. USSR* **1969**, *5*, 523–525.

9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]-inden-9-one (Triptindan-9-one, 13). Polyphosphoric acid (200 g, Merck, 85% P_4O_{10}) is heated to 50 °C and stirred vigorously with a mechanical stirrer as 16.3 g (50.0 mmol) of diketone 12[5a,18] is added. The initially yellow suspension is stirred and heated to 120 °C. Stirring for 12–60 h at this temperature is necessary to complete the reaction, depending on the quality of the PPA. The dark brown solution is cooled to 10 °C and diluted with water without allowing its temperature to rise above 30 °C. After neutralization with aqueous NaOH to pH 6, the solution is extracted several times with diethyl ether. The extracts are washed with water and dried with Na_2SO_4, and the solvent is removed. The solid residue is purified by recrystallization from MeOH/charcoal, yielding 14.1 g (91%) of colorless, fine crystals of mp 183 °C.[41] R_f ($CHCl_3$): 0.70. IR (KBr): 2920, 2839 (CH), 1698 (C=O) cm^{-1}. ^1H NMR (300 MHz): δ 7.94 (d; $^3J_{8-7}$ = 7.69 Hz; 1 H; 8-H), 7.76 (d; ^3J = 7.32 Hz; 2 H; 4,15-H), 7.71 (d; $^3J_{5-4}$ = 7.68 Hz; 1 H; 5-H), 7.63 (t; ^3J = 7.65 Hz; 1 H; 6-H), 7.34 (t; ^3J = 7.65 Hz; 1 H; 7-H), 7.27–7.11 (m; 6-H; 1,2,3,12,13,14-H), *AB* (δ_A 3.57, δ_B 3.29, J_{AB} = −17.24 Hz; 4 H; 10,11-H). UV (*n*-heptane): λ_{max} (log ϵ) 224.8 (4.26), 242.0 (4.08), 262.5 (3.40), 270.0 (3.53), 276.2 (3.59), 291.0 (3.29), 298.4 (3.29). MS: *m/z* 308 (100, $M^{\bullet+}$), 309 (24), 279 (17), 217 (17), 202 (12), 91 (11). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.86; H, 5.23.

9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]indene (Triptindan, 1). A suspension of 80.0 mg of 10% Pd/C in a solution of 616 mg (2.00 mmol) of **13** in 100 mL of EtOH is shaken in a Parr apparatus at rt under hydrogen pressure (3.6 bar) for 24 h. The solid residue (500 mg) obtained after removal of the catalyst and the solvent is recrystallized from MeOH, giving 450 mg (76%) of colorless crystals, mp 191 °C (lit.[6b] mp 192 °C). R_f (hexane/EtOAc): 0.90. The product is identical by ^1H NMR and mass spectra with the compound described earlier.[6b] IR (KBr): 3065, 3021, 2923, 2839 (CH), 1471, 753, 726. MS: *m/z* 294 (35, $M^{\bullet+}$), 204 (18), 203 (100), 202 (22).

10,11-Dibromo-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]inden-9-one (15). A solution of 5.30 g (17.2 mmol) of **13** in 50.0 mL of dry CCl_4 is stirred and heated under reflux at 35.0 mL of a 1 M solution of Br_2 (35 mmol) in CCl_4 is added through a dropping funnel while irradiating the ketone solution with a 500-W photolamp. After the addition is complete, irradiation is continued for 30 min under reflux, during which time a white solid precipitate is formed and HBr is liberated. After being cooled to rt, the solvent and remaining HBr are removed in vacuo. Ketone **15** is obtained as a colorless powder, which is pure according to TLC and can be used directly in the subsequent oxidation step, yield 7.50 g (93%). R_f ($CHCl_3$): 0.85. IR (KBr): 3070 (CH), 1711 (C=O), 756 cm^{-1}. ^1H NMR (300 MHz): δ 7.90 (d; $^3J_{8-7}$ = 7.71 Hz; 1 H; 8-H), 7.78 (d; $^3J_{5-6}$ = 6.60 Hz; 1 H; 5-H), 7.71 (t; ^3J = 7.70 Hz; 1 H; 6-H), 7.65 (d; ^3J = 7.61 Hz; 2 H; 4,15-H), 7.37–7.25 (m; 6 H; 1,2,3,12,13,14-H), 6.24 (s; 1 H; 10[11]-H), 6.22 (s; 1 H, 11[10]-H). MS: *m/z* 385/387 (94/97, ($M^{\bullet+}$ − Br)), 386/388 (26/22), 307 (25), 306 (100), 305 (38), 278 (47), 277 (61), 276 (87), 274 (23), 202/200 (24/26), 153 (37), 138 (39). Anal. Calcd for $C_{23}H_{14}Br_2O$: C, 59.26; H, 3.03. Found: C, 58.90; H, 2.95.

11-Bromo-9*H*,10*H*-4b,9a-([1,2]benzenomethano)indeno-[1,2-*a*]indene-9,10-dione (16). Under the conditions given for **15**, 8.00 mL of a 1 M solution of Br_2 in CCl_4 is added to a solution of 620 mg (2.00 mmol) of **13** in 25 mL of CCl_4 and reacted as described previously. After workup, a mixture of two products is obtained (R_f ($CHCl_3$) 0.85 (**15**), 0.50 (presumably **14**)) and separated by MPLC with $CHCl_3$ as the eluent. Besides 350 mg (40%) of **15**, 120 mg of a colorless powder is obtained with R_f 0.15, which is identified, according to ^1H NMR and mass spectrometry, as diketone **16**. MS: *m/z* 321 (100, $(M - Br)^+$), 322 (30), 265 (45), 263 (45), 187 (14), 189 (16). ^1H NMR (300 MHz): δ 8.57 (d; ^3J = 7.76 Hz; 1 H; 8[12]-H), 8.45 (d; ^3J = 7.77 Hz; 1 H; 12[8]-H), 8.31 (d; ^3J = 7.56 Hz; 1 H), 7.84 (t; ^3J= 7.87 Hz; 2 H), 7.77 (t; ^3J = 7.78 Hz; 2 H), 7.70–7.35 (m; 5 H), 6.06 (s; 1 H; 11-H).

9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]-indene-9,10,11-trione (Triptindan-9,10,11-trione, 3). To a solution of 7.50 g (16.1 mmol) of **15** in 70 mL of DMSO (Merck, p.a.) is added 6.50 g (46.0 mmol) of Na_2HPO_4, 1.65 g (12.0 mmol) of KH_2PO_4, and 500 mg (4.60 mmol) of NaBr, and the suspension is stirred and heated to 80–100 °C for 8 h. The oxidation is controlled by TLC ($CHCl_3$/EtOAc). After completion, the mixture is cooled to rt and poured into 200 mL of water, and the aqueous solution is extracted several times with $CHCl_3$. The organic phase is washed with water and saturated aqueous NH_4Cl, dried with Na_2SO_4, and concentrated to dryness. Triketone **3** is obtained as an almost colorless solid (crude yield 5.36 g, 99%), which can be recrystallized from 700 (!) mL of THF giving 4.28 g (79%) as a colorless powder with mp > 360 °C. R_f ($CHCl_3$/EtOAc): 0.55. IR (KBr): 3030 (CH), 1760, 1695 (C=O) cm^{-1}. ^1H NMR (300 MHz): δ 8.18 (d; ^3J = 7.69 Hz; 3 H; 1,8,12-H), 7.75 (t; ^3J = 7.14 Hz; 3 H; 3,6,14-H), 7.74 (d; ^3J = 7.39 Hz; 3 H; 4,5,15-H), 7.27 (t; ^3J = 7.20 Hz; 3 H; 2,7,13-H). ^{13}C NMR (75 MHz): δ 184.84 (C-9,10,11), 153.34 (quart. C), 136.46 (tert C), 134.12 (quart. C), 129.98, 125.90, 124.63 (tert C), 86.28, 61.32 (C-4b,9a). MS: *m/z* 336 (100, $M^{\bullet+}$), 337 (24), 308 (41), 280 (40), 252 (26), 250 (23), 125 (18), 113 (11), 76 (10). UV (*n*-heptane/EtOH (60:40)): λ_{max} (log ϵ) = 223.0 (4.21), 245 (4.21), 264.8 (4.06), 283.0 (3.46). Anal. Calcd for $C_{23}H_{12}O_3$: C, 82.13; H, 3.60. Found: C, 81.85; H, 3.68.

9,10,11-Tris(methylene)-9*H*,10*H*-4b,9a-([1,2]benzenomethano)indeno[1,2-*a*]indene (19). A suspension of 1.68 g (5.00 mmol) of trione **3** in 100 mL of dry diethyl ether is stirred under nitrogen atmosphere, as 30.0 mL (60.0 mmol) of a 2 M solution of methylmagnesium bromide in the same solvent is added by injection through a septum rubber. A clear, red solution and an amorphous precipitate form. The mixture is heated to reflux for 1 h and stirred at rt overnight. After cautious hydrolyzation with small portions of water and acidification with diluted HCl, the mixture is extracted several times with diethyl ether, the organic phase is washed with saturated aqueous NH_4Cl, and the solvent is removed. The fluffy residue is resolved in toluene, *p*-toluenesulfonic acid is added (≃30 mg), the mixture is heated to reflux temperature in a rotary evaporator, and the azeotrope is distilled off. After being cooled to rt the remaining solution is washed with saturated aqueous $NaHCO_3$, dried with Na_2SO_4, and concentrated to dryness. The crystalline residue is recrystallized from $CHCl_3$/hexane, giving 1.30 g (79%) of **19** as colorless platelets, mp 207 °C. R_f ($CHCl_3$): 0.90. IR (KBr): 3064, 3038 (CH), 1637 (C=C), 883, 751 cm^{-1}. ^1H NMR (300 MHz): δ 7.71 (d; ^3J = 7.05 Hz; 3 H; 1,8,12-H), 7.44 (d; ^3J = 7.35 Hz; 3 H; 4,5,15-H), 7.31–7.17 (m; 6 H; 2,3,6,7,13,14-H), 5.73 (s; 3 H; 9′,10′,11′-H_A), 5.53 (s; 3 H; 9′,10′,11′-H_B). MS: *m/z* 330 (100, $M^{\bullet+}$), 331 (30), 327 (13), 326 (15), 316 (14), 315 (42), 314 (13), 313 (24), 303 (17), 302 (41), 226 (10), 165 (8, M^{2+}). Anal. Calcd for $C_{26}H_{18}$: C, 94.52; H, 5.48. Found: C, 94.10; H, 5.46.

9,10,11-Tris(benzylidene)-9*H*,10*H*-4b,9a-([1,2]benzenomethano)indeno[1,2-*a*]indene (21). A suspension of 336 mg (1.00 mmol) of trione **3** in 30 mL of dry benzene is stirred under nitrogen atmosphere, as 11.0 mL (30.8 mmol) of a 2.8 M solution of benzylmagnesium bromide in diethyl ether is added by injection through a septum rubber. The mixture immediately turns dark brown under complete dissolution of the educt and is heated to reflux for 3 h. After being cooled to rt the mixture is cautiously hydrolyzed with water, and the magnesium salts are dissolved with diluted aqueous HCl. The organic layer is separated, washed with saturated aqueous NH_4Cl, and dried with Na_2SO_4. The solvent is removed, and 1,2-diphenylethane, as a byproduct, is distilled off in a Kugelrohr apparatus at 120 °C (15 Pa). The yellow oil thus obtained (560 mg, 92%; R_f (CH_2Cl_2/EtOAc 95:5) 0.32) is directly subjected to dehydration. The crude 9,10,11-tribenzyltriptindan-9,10,11-triol (**20**) is dissolved in 20 mL of DMSO (Merck, p.a.) and stirred at 160 °C for 20 h under nitrogen atmosphere. After being cooled to rt and dilution with water, the mixture is extracted several times with petroleum ether/diethyl ether. The combined organic phases are washed with water and saturated aqueous NaCl and dried with Na_2SO_4. After removal of the solvents, a dark brown oil remains, which is filtered as a $CHCl_3$ solution through silica gel. By using MPLC, the fraction with R_f 0.90 ($CHCl_3$/hexane 7:3) is separated as a colorless oil and identified as **21** (180 mg, 32%). IR (KBr): 3059, 3022, 2925 (CH), 1597 (C=C), 771, 755, 713, 697 cm^{-1}. ^1H NMR (300 MHz): δ 7.69 (d; ^3J = 7.52 Hz; 3 H), 7.40–7.12 (m, 22 H), 7.25 (s; 3 H; olefinic H), 6.97 (t; ^3J = 7.56 Hz; 3 H). ^{13}C NMR (75 MHz): δ 147.97 (C-9,10,11), 143.64 (C-4a,4c,15a), 139.25 (tert C), 137.97 (C-8a,10a,11a), 129.64 (C-9^1,10^1,11^1), 128.85, 128.69, 128.42, 128.01,

(41) Schuster, A. Diploma Thesis, Universität Bielefeld, 1987.

127.10, 126.89, 126.72 (tert C), 125.92 (tert C, C-9^6,10^6,11^6), 80.62 (C-4b), 71.17 (C-9a), MS: m/z 558 (100, $M^{\cdot+}$), 559 (48), 468 (24), 467 (58), 390 (22), 389 (49), 379 (12), 376 (10), 302 (11), 201 (15), 91 (20). Anal. (by high-resolution mass spectrometry) Calcd for $C_{44}H_{30}$: 558.7279. Found: 558.7278.

9*H*,10*H*-4b,9a-([1,2-]Benzenomethano)indeno[1,2-*a*]-indene-9,10,11-trispirocyclopropane (22). A solution of 460 mg (1.40 mmol) of triene **19** in 75.0 mL of benzene is stirred under nitrogen atmosphere, as 28.0 mL of a 1 M solution of diethylzinc (28.0 mmol) in heptane (Merck–Schuchardt) is injected through a septum rubber. Stirring is continued for 5 min, and a solution of 7.70 g (28.7 mmol) of diiodomethane (Merck) in 20.0 mL benzene is added dropwise within 15 min, while the mixture is warmed up to 50–60 °C. After the mixture is cooled to rt, a stream of air, which has been dried by passing through molecular sieves (3 Å) and then through P_4O_{10} (Sicapent, Merck), is allowed to pass over the reaction mixture for 1–2 h. The completion of the reaction is determined by TLC. After dilution with 50 mL of pentane, the zinc oxide precipitated is dissolved with diluted aqueous HCl, and the layers are separated. The aqueous phase is extracted with benzene, the combined organic solutions are washed with water and saturated aqueous NaCl, dried with Na_2SO_4, and concentrated to dryness. A solution of the brownish, solidifying residue in hexane/$CHCl_3$ azeotrope is filtered over silica gel and purified by MPLC. The trispirane **22** is obtained as colorless powder (378 mg, 73%), which is recrystallized from $CHCl_3$/hexane, mp 308–310 °C. R_f ($CHCl_3$/hexane azeotrope): 0.82. IR (KBr): 3059, 3032, 2991 (CH), 1477, 1458 (δ CH), 1016, 753 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 7.63 (d; ^3J = 6.32 Hz; ^4J = 1.99 Hz; 3 H; 4,5,15-H), 7.12 (m; 6 H; 2,3,6,7,13,14-H), 6.72 (d; ^3J = 6.65 Hz; ^4J = 1.95 Hz; 3 H; 1,8,12-H), 1.22 (m; 3 H; 9^2,10^2,11^2-H_{out}), 1.13 (m; 3 H; 9^2,10^2,11^2-H_{in}), 0.95 (m; 3 H; 9^1,10^1,11^1-H_{in}), 0.02 (m; 3 H; 9^1,10^1,11^1-H_{out}). ^{13}C NMR (75 MHz): δ 148.76, 144.38 (C-4a,4c,8a, 10a,11a-C), 127.19, 126.24, 123.58, 118.06 (sec C), 74.83 (C-4b), 67.46 (C-9a), 30.30 (C-9,10,11), 15.38 (C-9^1,10^1,11^1[out]), 6.48 (C-9^2,10^2,11^2[in]). MS: m/z 372 (100, $M^{\cdot+}$), 373 (30), 357 (29), 345 (11), 344 (41), 343 (64), 342 (16), 341 (15), 331 (14), 330 (38), 329 (27), 328 (35), 327 (32), 326 (23), 316 (40), 315 (51), 303 (21), 302 (31), 239 (24), 228 (12), 215 (17), 164 (14), 163 (26), 157 (24), 150 (16). Anal. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49. Found: C, 94.00; H, 6.21.

Isomerization of 22, Ethyltribenzocentropentaquinene (24). Trispirane **22** (372 mg, 1.00 mmol) is dissolved in 15 mL of CH_2Cl_2 under nitrogen atmosphere and cooled to 0 °C under stirring. One drop of trifluoromethanesulfonic acid is added through a septum rubber, and stirring is continued for 20 min. After addition of saturated aqueous Na_2CO_3, the aqueous layer is separated and extracted with CH_2Cl_2, and the organic extract is dried with Na_2SO_4. The solvent is removed, and the oily residue is purified by MPLC ($CHCl_3$/hexane (72:28), v/v) yielding **24** as a colorless oil. R_f ($CHCl_3$/hexane 7:3): 0.80. ^1H NMR (300 MHz): δ 7.70 (d; ^3J = 7.8 Hz; 1 H, arom *endo*-H), 7.67 (d; ^3J = 7.8 Hz; 1 H; arom *endo*–H), 7.54 (d; ^3J = 5.8 Hz; 1 H; arom *endo*–H) (doublets split by additional ^4J-coupling), 7.30–7.05 (m; 9 H; arom H), *ABX* system *X* part, δ_X = 5.74, J_{AX} = 1.72 Hz, J_{BX} = 3.66 Hz; 1 H; olefinic H, *AB* part, δ_A = 3.21, δ_B = 3.00, J_{AB} = –16.9 Hz; allylic CH_2), 2.45–1.60 (m; 6 H; endocyclic CH_2, ethyl-CH_2), 0.67 (t; ^3H = 7.5 Hz; 3 H; $-CH_3$). MS: m/z 372 (100, $M^{\cdot+}$), 373 (31), 357 (17), 343 (48), 203 (16).

Monomethylene Adduct (Presumably 30) of Triptindan-9,10,11-trione (3). In analogy to the procedure given in the following text for **31**, the DMSO/THF solution of the ylide prepared from 70.0 mg of NaH (2.42 mmol, 80% in paraffin) and 484 mg (2.42 mmol) of trimethylsulfonium iodide in 1.8 mL of DMSO is reacted with 672 mg (2.00 mmol) of trione **3** in 8 mL of DMSO/THF. After being stirred for 24 h at rt, the mixture is poured into a rapidly stirred suspension of diethyl ether and saturated aqueous NH_4Cl and cooled to 0 °C. The ether layer is washed with water and dried with Na_2SO_4. The solvent is removed in vacuo at rt (see the following text), and the colorless, crystalline residue is purified by MPLC (heptane/EtOAc (1:1)), yielding 100 mg (14%) of colorless crystals. R_f (heptane/EtOAc): 0.70, impurity at 0.80, educt **3** at 0.43. ^1H NMR (300 MHz, acetone-d_6): δ 8.37 (d; ^3J = 8.13 Hz; 1 H; arom *endo*-H (cf. ref 10b)), 8.15 (d; ^3J = 7.79 Hz; 2 H; arom *endo*-H), 7.92–7.30 (m; 9 H; arom H), 6.06 (s; 1 H; methylene-H), 5.73 (s; 1 H, methylene-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.86 (carbonyl-C), 160.83, 153.83, 144.69, 143.99, 138.89 (quart. C), 137.32, 135.60 (tert C), 135.43, 131.48 (quart. C), 130.56, 129.73, 129.37, 128.79, 126.38, 124.85, 122.38 (tert C), 120.55, (quart. C), 112.73 (methylene-C), 92.42 (quart. C), 55.24 (quart. C). MS: m/z 350 (100, $M^{\cdot+}$), 351 (26), 322 (15), 305 (70), 294 (23), 265 (59), 263 (29), 132 (24).

9-Methylene-9*H*,10*H*-4b,9a-([1,2]benzenomethano)-indeno[1,2-*a*]indene 9,16-Epoxide (31). In a predried reaction apparatus, 346 mg (12.0 mmol) of NaH (80% in paraffin) is washed three times with 20 mL of dry pentane under nitrogen atmosphere. The residual pentane is removed in vacuo, and the apparatus is refilled with nitrogen. DMSO (8.0 mL, Merck, p.a.) is injected through a rubber septum onto the NaH powder and reacted to give the methylsulfinyl carbanion under evolution of hydrogen. After cooling to rt, the mixture is diluted with 10 mL of dry THF and further cooled to –10 °C. A solution of 2.45 g (12.0 mmol) of trimethylsulfonium iodide in 9.6 mL of DMSO is injected quickly into the suspension. Stirring is continued for 1 min at –10 °C, as a solution of 1.54 g (5.00 mmol) of triptindan-9-one (**13**) in 10.0 mL of DMSO/THF (8:10 v/v) is added within 3 min. Upon addition of the ketone, the suspension turns yellow and slight evolution of gas is observed. Stirring is continued for 10 min at –10 °C and then for 30–60 min without external cooling. After addition of 100 mL of water, the solution is extracted several times with diethyl ether, and the organic phase is washed with water and dried with Na_2CO_3. The product is isolated by removal of the solvent in vacuo without warming (!) and without recrystallization because of rapid decomposition at elevated temperatures. Epoxide **31** is obtained in almost quantitative yield (1.61 g) as a grayish powder. R_f (EtOAc/heptane (3:7): 0.45. IR (KBr): 3063, 2928, 2845 (CH), 1601 (C=C), 916 (CO), 756 cm^{-1}. ^1H NMR (300 MHz): δ 7.93 (d; ^3J = 7.55 Hz; 1 H; 8-H), 7.86 (dd; ^3J = 6.73 Hz, ^4J = 1.72 Hz; 2 H), 7.38 (t; ^3J = 7.41 Hz; 1 H), 7.28–7.08 (m; 8 H), 3.14 (s; 2 H; 9[10]-H), *AB* (δ_A = 3.49, δ_B = 3.33, J_{AB} = 4.43 Hz; 2 H; 9^1-H), *AB* (δ_A = 3.25, δ_B = 2.79, J_{AB} = –16.62 Hz; 2 H; 10[9]-H). MS: m/z 322 (45, $M^{\cdot+}$), 323 (12), 304 (19), 294 (29), 293 (100), 291 (20), 289 (14), 278 (12), 215 (28), 203 (55), 202 (34), 178 (17), 138 (10), 115 (12), 91 (27). Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 88.54; H, 6.00.

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