Preparation and Properties of Centrally Bridgehead-Substituted Hexacyclo[4.4.0.0^{2,1}.0^{3,5}.0^{4,8}.0^{7,9}]decanes ("Diademanes") and Related $(CH)_{10}$ Hydrocarbons

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Abstract: 6-Trimethylsilyl- (**1b**), 6-hydroxymethyl- (**1e**), and 6-methyldiademane (**1f**) have been prepared by irradiation of the corresponding snoutene derivatives, in 23, 2.8, and 17% yields, respectively, together with the isomeric 1-trimethylsilyl- (**10b**) and 1-methyldiademane (**10f**) (8 and 2% yields, respectively). The starting 4-trimethylsilyl- (**9b**) and 4-(trimethylsilyloxymethyl)-snoutene (**9d**) were prepared from the correspondingly substituted cyclooctatetraenes **4b** and **4c** in several steps in 20 and 8% overall yields, respectively. Upon heating, as well as under the conditions of gas-chromatographic separation, diademanes **1b**, **10b**, **1f**, and **10f** rearranged into the corresponding C10- and C1-substituted triquinacenes **3b**, **3f**, **11b**, and **11f**, respectively. Rough kinetic measurements of these rearrangements indicate some acceleration of the reaction caused by the presence of a methyl substituent and retardation by that of a trimethylsilyl substituent, relative to the parent diademane **1a**. At this insufficient precision, however, the activation energies (E_a) of 29.0 and 28.1 kcal mol^{-1}, respectively, are essentially the same as that reported for **1a** (28.3 kcal mol^{-1}). An X-ray crystal structure analysis of trimethylsilylsnoutene **9b** revealed a significant lengthening of the distal (with respect to the substituent) bond (1.534 versus 1.505 Å) in the unsubstituted cyclopropane ring. In the substituted cyclopropane ring, the two proximal bonds are lengthened (1.530 Å) and the distal bond is slightly shortened 1.492 Å). This indicates a small, but significant electron-withdrawing effect of the trimethylsilyl group in **9b**. An X-ray crystal structure analysis of 6-hydroxymethyldiademane **1e** showed pronounced alternation of the bond lengths in the six-membered ring, with 1.494(4) between and 1.539(4) Å within the three cyclopropane moieties, in close agreement with computations at different theoretical levels. This structural feature corroborates a predisposition of the tris-σ-homobenzene skeleton of this molecule in the ground state to undergo the facile $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversion to the triquinacene skeleton observed for the parent diademane **1a**, its derivative **1b** and **1f**, as well as for other tris-σ-homobenzene derivatives.

Keywords: alkenes · hydrocarbons · isomerization · polycycles · strained molecules · structure elucidation

Introduction

Among the members of the $(CH)_{10}$ hydrocarbon family, which—like other $(CH)_n$ hydrocarbon families—is known for its multiple photochemical and thermal rearrangements,[1, 2] the one nick-named "diademane" (hexacyclo-[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane, **1a**[3]) draws the eye because of its molecular shape, resembling that of a closed crown. Diademane **1a** is also remarkable because of its facile thermal rearrangement leading to triquinacene **3a**, in which the C_{3v} symmetry of the precursor is retained.[4] It has been proposed that this rearrangement is a concerted $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversion, in which three cyclopropane σ-bonds are opened and three π-bonds are formed simultaneously (Scheme 1).

According to MINDO/3[5] and B3LYP/6-311+G**[6] calculations, the transition structure **2** of this rearrangement has the same C_{3v} symmetry as the starting material **1a** and the product **3a**. To further test for this concept, we have prepared a number of centrally bridgehead-substituted derivatives. With the purpose of answering the important question of

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Scheme 1. Rearrangement of diademane **1a** into triquinacene **3a**.

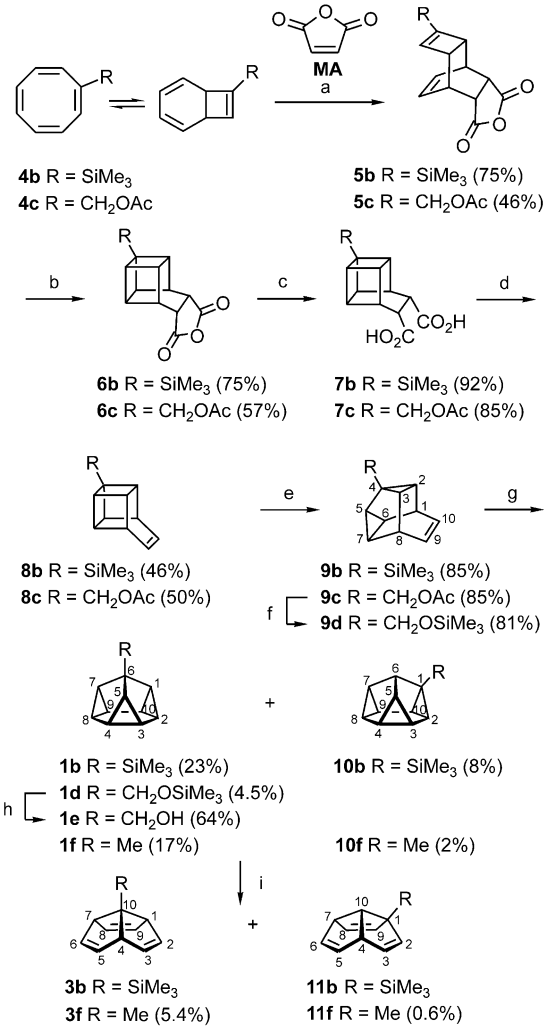
whether the characteristic cycloreversion is preexpressed in the ground-state structure of the diademane skeleton, efforts were made to determine the crystal structure of a C_{3v}-symmetric derivative of **1a** by X-ray diffraction, and finally met with success.

Results and Discussion

In an effort to investigate the thermodynamic and structural driving forces for the rearrangements within the $(CH)_{10}$ hydrocarbon family with a broader scope,[6a, 7] the recently elaborated in situ crystallization technique for compounds that form plastic phases[8] was applied and gave good results for basketene. However, X-ray diffraction results for a single crystal of diademane **1a** grown by careful heating with the IR laser (only to about 60 °C, in order to avoid rearrangement to **3a**) showed a tetrahedrally disordered structure in which the apical C atom of the diademane structure is positioned in each three-membered ring.[7] To overcome this difficulty, diademane derivatives with a substituent at the bridgehead position C6 were prepared. These derivatives were designed to retain the overall C_{3v} symmetry of the molecule **1a**, and possibly to be more suitable for X-ray crystal structure analysis. Towards this goal, a methyl, a trimethylsilyl, and eventually a hydroxymethyl group were chosen as the substituents.

Preparation of C6-substituted diademanes: The only method of preparing diademane **1a** is by long-term irradiation of pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (snoutene) **9a** (R = H) at low temperature.[4, 9] Snoutenes **9** with substituents at the 4-position should accordingly lead to C6- and/or C1-substituted diademanes. Thus, in addition to that of the previously reported 4-methylsnoutene (**9f**),[10] the synthesis of 4-trimethylsilylsnoutene (**9b**) and 4-(trimethylsilyloxymethyl)-snoutene (**9d**) were carried out according to the methodology developed for the preparation both of unsubstituted snoutene itself and of 4-methylsnoutene (**9f**).[10] This methodology is based upon the pioneering finding of Reppe et al.[11] that cyclooctatetraene (COT, **4**; R = H) is capable, through its bicyclo[4.2.0]octatriene valence tautomer,[12] of undergoing a Diels–Alder cycloaddition with dienophiles such as maleic anhydride (MA), furnishing the tricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic acid anhydride **5** (R = H).

In 1966, this compound was transformed independently by three groups—Dauben et al.,[13a] Masamune et al.,[13b] and Lehn et al.[13c]—in two steps into basketene **8a** (R = H), which underwent isomerization into snoutene **9a** (R = H) under the action of silver salts[14] (for further improvements in these preparations see also refs. [4, 15]). The starting materials, trimethylsilyl- (**4b**)[16] and (acetoxymethyl)cyclooctatetraene (**4c**) were prepared from the known bromocyclooctatetraene[17] and cyclooctatetraenylmethanol,[18] respectively, by established procedures (see Experimental Section). Prolonged heating of solutions of **4b** or **4c** with maleic anhydride in benzene afforded the cycloadducts **5b** and **5c** in 75 and 46% yields, respectively (Scheme 2), which were transformed



Scheme 2. Preparation of substituted diademanes **1b**, **1d**, **1e**, and **1f** and their thermal isomerization into substituted triquinacenes **3b**, **3f**, **11b**, and **11f**. a) C_6H_6, 80 °C, 36–48 h; b) C_6H_6/acetone, *hν*, 20 °C, 48 h; c) $NaHCO_3$, H_2O, 20 °C, then 12 N HCl, 0 °C; d) $Pb(OAc)_4$, pyridine, 55 °C, 3 h; e) $AgNO_3$, MeOH, 50 °C, 48 h; f) aq. 10% NaOH, 20 °C, 3 h, then Me_3SiCl/Et_3N, CH_2Cl_2, 20 °C, 2 h; g) pentane, *hν*, −65 °C, 72 h; h) TBAF, THF, 20 °C 15 min; i) gas-chromatographic separation.

into the corresponding basketane derivatives **6b** and **6c** by acetone-sensitized photocyclization. Compounds **6b** and **6c** were purified by crystallization and, after hydrolysis to the corresponding diacids **7b** and **7c**, were decarboxylated with lead tetraacetate to yield 4-trimethylsilyl- and 4-(acetoxymethyl)basketenes **8b** and **8c** in 32 and 24% yields, respectively, over three steps. Isomerization of **8b** and **8c** with silver nitrate in anhydrous methanol at 50 °C gave 4-trimethylsilyl-(**9b**) and 4-(acetoxymethyl)snoutene (**9c**), each in 85% yield after column chromatography.

With the targets of C6-substituted diademanes **1** in mind, it was crucial that the unsubstituted cyclopropane moiety in the

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substituted snoutenes **9** should participate in the intramolecular photochemical $[\sigma_s^2+\pi_s^2]$ cycloaddition.[19] Irradiation of 4-methylsnoutene **9f** in pentane solution at $-65\,^{\circ}C$ for 72 h yielded the two regioisomeric diademanes **1f** and **10f** in a ratio of 8:1 in favor of the desired isomer. As the attempted separation of the photoproducts from the starting material **9f** after conversion of the latter into the epoxide[4] was not successful, compound **1f** had to be isolated by preparative gas chromatography. Under the applied conditions, complete isomerization of diademane **10f** and partial reorganization of **1f** into the corresponding triquinacenes **11f** and **3f**, respectively, occurred.

Under the same photolytic conditions, 6-(trimethylsilyl)- (**1b**) and 1-(trimethylsilyl)diademane (**10b**) were obtained from the corresponding snoutene **9b** as a 3:1 mixture after separation from **9b** by epoxidation of the latter with *m*-chloroperbenzoic acid. Even though the mixture of **1b** and **10b** was solid, **1b** could not be purified either by crystallization or by any chromatographic method. Upon attempted GC separation, complete rearrangement of both isomers to the corresponding triquinacenes **3b** and **11b** could not be avoided.

Because the solubility of 4-(acetoxymethyl)snoutene (**9c**) in pentane was not good enough, diethyl ether was used as a co-solvent for its attempted photochemical isomerization. However, the corresponding diademane derivative could not be isolated from the reaction mixture, neither could the starting material **9c** be recovered. This was taken to indicate that the acetyl protecting group is not inert under the photolytic conditions. Therefore, **9c** was converted in two steps to the trimethylsilyloxymethyl derivative **9d**. This could indeed be photoisomerized to the target molecule **1d**, albeit in low yield (4.5%). After protiodesilylation, 6-(hydroxymethyl)diademane (**1e**), which crystallized from acetone furnishing crystals of good quality for an X-ray structure analysis, was obtained. However, the overall yield of **1e** from **9c** was only 2.3%.

Kinetics of thermal isomerizations: The series of prepared diademane derivatives **1a**, **1b**, and **1f** offered itself for the investigation of the substituent effects on the kinetics of the thermal rearrangement of the diademane skeleton. Although 6-(trimethylsilyl)diademane (**1b**) was not obtained in pure form, its thermal isomerization could be monitored by ^{1}H NMR spectroscopy, because its signals were well separated from those of **10b**. Comparison of the kinetic parameters determined for **1b** and for 6-methyldiademane (**1f**) with those for the parent diademane **1a** (see Table 1) shows that the π-electron-withdrawing trimethylsilyl group[20] causes—as far as the rate coefficients are concerned—a slight retardation of the $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversion, whereas the σ-electron-donating methyl group leads to an even smaller acceleration. However, within the limits of error of this current study, the measured Arrhenius activation energies of 29.0 ± 1.0 and 28.1 ± 1.0 kcal mol^{-1} are virtually the same as that reported for the parent diademane **1a** (28.3 ± 1.0 kcal mol^{-1}).[4a, 9] This is due to the lack of precision in these kinetic measurements, with only three points on each correlation line. Irrespective of that, the conclusion can be drawn that at least the presence of a trimethylsilyl or a methyl group at the 6-position does not significantly distort the skeleton of diademane and, therefore, does not significantly alter the activation barrier for rearrangement to the respective triquinacene derivatives.

Table 1. Kinetic parameters for the reorganization of diademane (**1a**), 6-trimethylsilyl-diademane (**1b**), and 6-methyldiademane (**1f**) into the corresponding triquinacenes **3a**, **3b**, and **3f**, respectively.

Diademane	T [°C]	$10^5\,k$ [s^{-1}]	$t_{1/2}$ [min]	E_a [kcal mol^{-1}]
1a[a]	80	6.5	177.6	
	90	17.9	64.5	28.3 ± 1.0
	100	53.8	21.5	
1b[b]	80	4.9	236.0	
	90	14.8	78.0	28.1 ± 1.0
	100	42.0	27.5	
1f[b]	80	9.8	118.0	
	90	30.4	40.0	29.0 ± 1.0
	100	90.0	12.8	

[a] Reference [4a,9]. [b] This work.

Single-crystal X-ray structure investigations: Single crystals of unsubstituted snoutene **9a** (R = H) could be obtained at $-55\,^{\circ}C$ by the in situ crystallization method.[8] However, according to DSC measurements, they were completely disordered and could not be used to derive structural details of the molecule.[7] Nevertheless, ab initio calculations performed for snoutene **9a** did not show any drastic deviations from the normal values of bond lengths and angles, except for a slight lengthening of four cyclopropane bonds (1.517 versus 1.504 Å for the other two).[7] On the other hand, the trimethylsilyl derivative **9b**, upon in situ crystallization,[21] formed crystals of appropriate quality. According to the X-ray crystal structure analysis of **9b** (Figure 1), the bonds **c** in

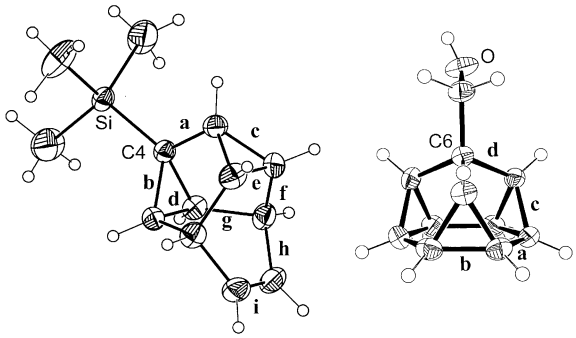

Figure 1. Structures of 4-(trimethylsilyl)pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (4-trimethylsilylsnoutene, **9b**, left) and 6-(hydroxymethyl)hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,7}.0^{8,10}]decane (6-(hydroxymethyl)diademane, **1e**, right) in the crystal.[25] Bond lengths [Å] (mean values based on assumed C_s symmetry for **9b** and C_{3v} symmetry for **1e**): **9b**: **a** = 1.515(4), **b** = 1.530(3), **c** = 1.505(3), **d** = 1.492(4), **e** = 1.534(3), **f** = 1.535(3), **g** = 1.533(3), **h** = 1.510(3), **i** = 1.320 (5). **1e**: see Table 2. For the numbering of the atoms see Scheme 2.

the unsubstituted cyclopropane moiety are virtually the same as in unsubstituted cyclopropane itself (**c** = 1.505(3) vs. 1.499(1) Å[22]), but bond **e** in the unsubstituted cyclopropane moiety is significantly lengthened (1.534(3) Å); this must be caused by the β-donating effect of the trimethylsilyl group.[23] In the substituted cyclopropane moiety, however, π electron withdrawal comes to play its role, so that the two proximal (with respect to the $SiMe_3$ group) bonds **b** are lengthened

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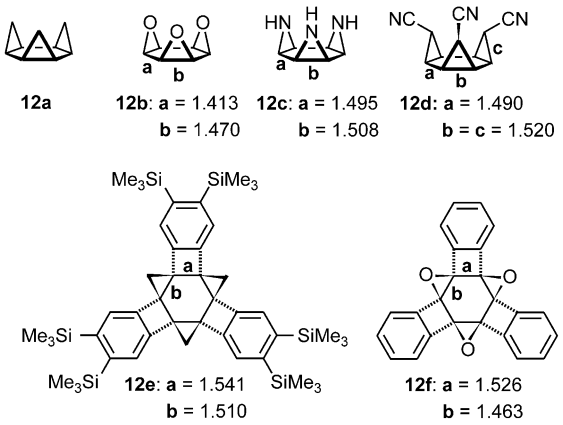
(1.530(3) Å) and the distal bond **d** is slightly shortened (1.492(4) Å).[24] This is in accord with the observed participation of the unsubstituted cyclopropane moiety in the photochemical intramolecular $[\sigma_s^2+\pi_s^2]$ cycloaddition leading from **9b** to **1b**.

The unsubstituted diademane **1a** and the centrally bridgehead-substituted derivatives **1b**–**f** are all bridged versions of the so-called tris-σ-homobenzenes. The nature of the bonds involved in such molecules and the favorable thermodynamics facilitate concerted $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversions. While the parent *cis*-[1.1.1]-tris-σ-homobenzene **12a** still remains elusive, a number of substituted and unsubstituted trishetera-*cis*-tris-σ-homobenzenes have been prepared, as well as the triscyano-*cis*-tris-σ-homobenzene **12d**,[26] the tris(benzocyclobutadieno)-*cis*-tris-σ-homobenzene **12e**,[27] and the trisoxa-*cis*-tris-σ-homobenzene **12f**,[27] and five of these (**12b**–**f**) could be characterized by X-ray crystal structure analysis (Scheme 3).



Scheme 3. Selected bond lengths [Å] of some known *cis*-tris-σ-homobenzene derivatives **12b**–**f**.[26, 27]

A comparison of these experimental data discloses one common feature in all these molecules, in that there is a modest, but significant bond-length alternation in the six-membered ring. For all three non-annelated compounds **12b**–**d**, the bonds between the three-membered rings are shorter than normal C–C σ bonds and those within the three-membered rings are longer than is usual in heteracyclopropanes[28] and cyclopropane derivatives.[24] This is particularly remarkable in **12d**, in which the cyano group on each cyclopropane ring should lead to a significant shortening of the three distal bonds **b**. The bond lengths in **12b**–**d** thus express the predisposition of these molecules to undergo the $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversion. The same mode of bond-length alternation has been predicted for diademane **1a** in the ground state by computations at various levels of theory starting from the first applied MINDO/3 method[5] and up to the recently published density functional theory results at the B3LYP/6–311+G** level.[6b] All these reveal a shortening of the bonds between the cyclopropane rings and a lengthening of those within them (see, however, ref. [29b]). According to the best available computations, the cyclohexane bonds within the cyclopropane moieties are 0.015 Å longer than those between them (Table 2), indicating that this molecule should also be predisposed in the ground state for the known reorganization to triquinacene **3a**.

Table 2. Comparison of experimentally determined bond lengths [Å] for 6-(hydroxymethyl)diademane (**1e**, averaged for three independent molecules) with calculated values for **1e** and for unsubstituted diademane **1a**: mean values for assumed C_s and C_{3v} symmetry, respectively (standard deviations in parentheses). See Figure 1.

Method (compound)	Bond type **a**	**b**	**c**	**d**
X-ray (**1e**)[a]	1.494(4)	1.539(4)	1.502(4)	1.559(4)
B3LYP/6–31G* (**1e**)[a]	1.510	1.523	1.511	1.567
B3LYP/6–311+G** (**1e**)[a]	1.510	1.523	1.508	1.566
MNDO (**1a**)[b]	–[g]	1.544	1.548	1.559
MINDO/3 (**1a**)[c]	1.525	1.535	1.539	1.565
6–31G* (**1a**)[d]	1.509	1.506	1.498	1.554
STO-3G (**1a**)[d]	1.518	1.512	1.505	1.561
PM3 (**1a**)[e]	1.513	1.517	1.496	1.545
RMP2/6–31G* (**1a**)[f]	1.502	1.519	1.509	1.552
B3LYP/6–311+G** (**1a**)[f]	1.508	1.523	1.512	1.561
B3LYP/6–31G* (**1a**)[a]	1.510	1.523	1.511	1.560

[a] This work. [b] Reference [30]. [c] Reference [5]. [d] Reference [29]. [e] Semiempirical method[31]. [f] Reference [6b]. [g] Not reported.

This effect is indeed experimentally observed in the skeleton of 6-(hydroxymethyl)diademane (**1e**, Table 2). The bond lengths in the six-membered ring alternate strictly, with 1.494(4) Å for the three bonds between the cyclopropane rings and 1.539(4) Å for the three within them. The other six cyclopropane bonds (1.502(4) Å) are shorter than the best calculated value and very close to the normal length of 1.499(1) Å in cyclopropane.[22] The experimentally determined value for bond **d** (1.559(4) Å) is the only one that almost completely agrees with the calculated value for diademane **1a**. The deviations between the experimentally determined bond lengths **a**–**d** and the best available computed ones can be attributed to the influence of the substituent at C6 and to crystal packing effects. The packing is mainly influenced by the formation of hydrogen bonds between the hydroxy groups of assemblies of 6-(hydroxymethyl)diademane molecules (Figure 2).

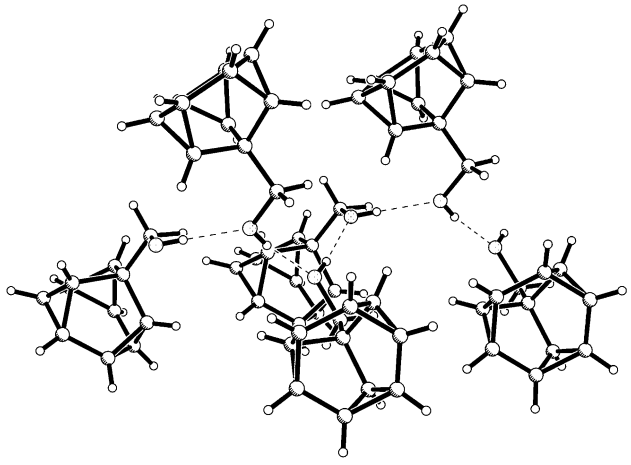


Figure 2. Molecular packing of 6-(hydroxymethyl)diademane (**1e**) in the crystal.

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However, the main trend in such molecules—shortened bonds between the three-membered rings and longer bonds within them—was correctly predicted by the calculations. Nevertheless, this experimental investigation disclosed a more pronounced alternation than the best available computation methods (i.e., the molecule is really predisposed to undergo the $[\sigma_s^2+\sigma_s^2+\sigma_s^2]$ cycloreversion). For comparison, the opposite alternation was observed for the tris(benzocyclobutadieno)-*cis*-tris-σ-homobenzene **12e** and the corresponding trisepoxide **12f** (Scheme 3), and, indeed, the former turned out to be relatively stable thermally (up to 340 °C), and the latter had to be heated to 180 °C before it underwent rearrangement, but without opening of the central six-membered ring.[27]

Experimental Section

General aspects: Bromocyclooctatetraene,[17] cyclooctatetraenylmethanol,[18] and 4-methylsnoutene (**9f**)[10] were prepared by the previously published procedures. Pentane was shaken with conc. sulfuric acid for 12 h, then with a 0.5 N solution of $KMnO_4$ in 3 M H_2SO_4 for 24 h, washed with diluted aq. oxalic acid and aq. $NaHCO_3$ (5%), dried ($MgSO_4$), and distilled from P_4O_{10}. Anhydrous diethyl ether, THF, and benzene were obtained by distillation from sodium benzophenone ketyl, CH_2Cl_2 and pyridine from CaH_2, and methanol from freshly prepared magnesium methoxide. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All operations in anhydrous solvents were performed under argon in flame-dried glassware. Organic extracts were dried over $MgSO_4$. The compositions of solvent mixtures are given as volume per volume. ^{1}H and ^{13}C NMR spectra were recorded at 250 and 270 MHz (^{1}H) and at 62.9, 100.6 MHz [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] on Bruker AM 250 and WH 270 instruments in $CDCl_3$ or C_6D_6 solutions, with $CHCl_3/CDCl_3$ or C_6D_5H/C_6D_6 as internal references; δ in ppm, J in Hz. IR spectra were recorded on Perkin–Elmer 297 and 299, and Bruker IFS 66 (FT-IR) spectrophotometers as KBr pellets or as oils between KBr plates. Mass spectra (EI) were measured with Varian MAT 112 and Finnigan MAT 95 spectrometers. Melting points were determined on a Büchi 510 capillary melting point apparatus, values are uncorrected. TLC analyses were performed on precoated sheets (0.25 mm Sil G/UV$_{254}$, Macherey–Nagel). Silica gel grade 60, 230–400 mesh (Merck), was used for column chromatography.

Trimethylsilylcyclooctatetraene[16] **(4b)**: *n*-Butyllithium (101 mmol, 44 mL of a 2.3 M solution in hexane) was added dropwise at −78 °C, under an atmosphere of argon, to a stirred solution of bromocyclooctatetraene[17] (18.3 g, 100 mmol) in anhydrous diethyl ether (100 mL). After additional stirring at −55 to −60 °C for 2 h, the reaction mixture was cooled to −78 °C, treated dropwise with a solution of Me_3SiCl (10.8 g, 100 mmol) in Et_2O (50 mL), and stirred for an additional 2 h at 0 °C. The reaction mixture was poured into ice-cold water (200 mL) and extracted with Et_2O (3 × 100 mL). The combined ethereal extracts were washed with water and aq. sat. $NaHCO_3$ solution (100 mL each), dried, and concentrated under reduced pressure to give 16.5 g (94%) of **4b** as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.30–5.70 (m, 7H; 7 × =CH), 0.10 ppm (s, 9H; 3 × CH_3).

Cyclooctatetraenylmethyl acetate (4c): DMAP (200 mg, 1.64 mmol, 2.8 mol%) and acetic anhydride (6.40 g, 5.91 mL, 62.7 mmol) were added under an atmosphere of argon to a solution of cyclooctatetraenylmethanol[18] (8.0 g, 59.6 mmol) in anhydrous pyridine (60 mL). The reaction mixture was stirred at ambient temperature for 3 h and was then poured into ice-cold water (300 mL); the mixture was extracted with hexane (3 × 100 mL). The combined organic layers were washed with aq. HCl (1 N) and sat. $NaHCO_3$ solutions (100 mL each), dried, and concentrated under reduced pressure. Vacuum distillation of the residue gave 9.50 g (90%) of **4c** as a colorless oil, b.p. 110 °C (15 Torr); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.00–5.70 (m, 7H; 7CH), 4.50 (s, 2H; OCH_2), 2.05 ppm (s, 3H; CH_3); IR (film): $\tilde{\nu}$ = 1740 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{12}O_2$ (176.2): C 74.97, H 6.87; found C 74.67, H 6.77.

Preparation of 3-substituted tricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic acid anhydrides 5b and 5c

General procedure GP 1: A stirred solution of the appropriate cyclooctatetraene derivative **4** (50 mmol) and maleic anhydride (MA) (62 mmol) in anhydrous benzene (50 mL) was heated at reflux for the indicated time under an atmosphere of argon. After cooling to ambient temperature and evaporation of the solvent to about 50% of its initial volume, diethyl ether (20 mL) was added, and the resulting solution was kept at 0 °C overnight. The precipitate was filtered off and recrystallized from Et_2O.

***endo*-3-(Trimethylsilyl)tricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic acid anhydride (5b)**: Anhydride **5b** (11.30 g, 75%) was obtained from **4b** (9.70 g, 55 mmol) and MA (6.60 g, 67.3 mmol) according to GP 1 after 36 h heating, as a colorless solid. M.p. 95 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.30 (s, 2H; 2=CH), 6.05–5.95 (m, 1H; =CH), 3.30–3.20 (m, 1H; CH), 3.10 (m, 3H; 3CH), 2.90 (m, 1H; CH), 2.80 (m, 1H; CH), −0.06 ppm (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 176.4 (2C), 148.0 (C), 133.0, 129.13, 129.1, 44.2, 44.16, 44.02, 44.0, 37.4, 36.8 (CH), −2.1 ppm (3CH_3); IR (KBr): $\tilde{\nu}$ = 3060, 3040, 2960, 1860, 1835, 1780, 1560, 1255, 1240, 1090, 930, 840 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{18}O_3Si$ (274.4): C 65.66, H 6.61; found C 65.27, H 6.47.

***endo*-3-Acetoxymethyltricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic acid anhydride (5c)**: Anhydride **5c** (6.40 g, 46%) was prepared as a colorless solid from **4c** (9.0 g, 51.1 mmol) and MA (6.60 g, 67.3 mmol) according to GP 1 after 48 h heating. M.p. 113–114 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.10–6.00 (m, 2H; 2=CH), 5.85 (brs, 1H; =CH), 4.40 (brs, 2H; OCH_2), 3.30 (m, 1H; CH), 3.20 (m, 1H; CH), 3.10 (m, 2H; 2CH), 2.80 (m, 1H; CH), 2.70 (m, 1H; CH), 2.10 ppm (s, 3H; CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 172.3 (2C), 170.4, 145.7 (C), 132.9, 129.3, 128.9 (CH), 60.4 (CH_2), 44.2, 43.6, 42.8, 39.5, 38.2, 36.3 (CH), 20.6 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 1840, 1770, 1730 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}O_5$ (274.3): C 65.69, H 5.14; found C 65.37, H 5.37.

Preparation of 4-substituted pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acid anhydrides 6b and 6c

General procedure GP 2: A solution of the appropriate diene **5** in a benzene/acetone mixture (9:1, 1800 mL) was irradiated in a water-cooled quartz reactor under an atmosphere of nitrogen with a 450 W medium-pressure mercury lamp (Hannovia 6515–34) at ambient temperature for 48 h. Evaporation of the solvent and recrystallization of the residue from ethyl acetate furnished compounds **6b** and **6c**.

4-(Trimethylsilyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acid anhydride (6b): Anhydride **6b** (8.3 g, 75%) was obtained from diene **5b** (11.0 g, 40.1 mmol) according to GP 2, as colorless crystals. M.p. 107–108 °C; ^{1}H NMR (270 MHz, C_6D_6): δ = 2.88 (m, 1H; CH), 2.80 (m, 1H; CH), 2.74 (m, 1H; CH), 2.65–2.47 (m, 4H; 4CH), 2.14 (m, 2H; 2CH), −0.06 ppm (s, 9H; 3CH_3); IR (KBr): $\tilde{\nu}$ = 2970, 1870, 1780, 1260, 1230, 1100, 990, 950, 855 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{18}O_3Si$ (274.4): C 65.66, H 6.61; found C 65.21, H 6.66.

4-Acetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acid anhydride (6c): Anhydride **6c** (14.3 g, 57%) was prepared from diene **5c** (25.0 g, 91.2 mmol) according to GP 2, as colorless crystals. M.p. 111–114 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.10 (s, 2H; CH_2), 3.40–3.00 (m, 9H; 9CH), 2.10 ppm (s, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 1850, 1780, 1730 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}O_5$ (274.3): C 65.69, H 5.14; found: C 65.51, H 5.10.

Preparation of 4-substituted pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acids 7b and 7c

General procedure GP 3: The appropriate anhydride **6** was vigorously stirred in an aq. sat. $NaHCO_3$ solution (150 mL) until it had completely dissolved. The solution was cooled to 0 °C, carefully acidified to pH ≈ 1–2 by addition of aq. 12 N HCl, and extracted with ethyl acetate (3 × 150 mL). The combined organic extracts were dried and concentrated under reduced pressure, and the residue was recrystallized from EtOAc.

4-(Trimethylsilyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acid (7b): Dicarboxylic acid **7b** (7.86 g, 92%) was obtained from its anhydride **6b** (8.0 g, 29.2 mmol) according to GP 3, as a colorless powder. M.p. 108–110 °C; ^{1}H NMR (270 MHz, C_6D_6): δ = 3.20 (m, 2H; 2CH), 3.00 (m, 1H;

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CH), 2.90 (m, 2H; 2CH), 2.80–2.59 (m, 2H; 2CH), 2.56 (m, 2H; 2CH), –0.12 ppm (s, 9H; 3CH_3), the signal of the OH protons was not detected; IR (KBr): $\tilde{\nu}$ = 3400, 2950, 1710, 1410, 1240, 840 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{20}O_4Si$ (292.4): C 61.61, H 6.89; found C 61.29, H 6.68.

4-Acetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-4,5-dicarboxylic acid (7c): Dicarboxylic acid **7c** (12.60 g, 85%) was prepared from its anhydride **6c** (14.0 g, 51 mmol) according to GP 3, as a colorless powder. M.p. > 300°C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.30 (brs, 2H; 2OH), 4.15 (s, 2H; OCH_2), 3.50–2.80 (m, 9H; 9CH), 2.10 ppm (s, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 3400, 1720 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{16}O_6$ (292.3): C 61.64, H 5.52; found C 61.31, H 5.30.

Preparation of 4-substituted pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-enes (basketenes) 8b and 8c

General procedure GP 4: Lead tetraacetate (68 mmol) was added to a solution of the appropriate dicarboxylic acid **7** (34 mmol) in anhydrous pyridine (100 mL), and the reaction mixture was stirred at 55°C under an atmosphere of argon for 3 h. After cooling to ambient temperature, the reaction mixture was poured into an ice-cold aq. HNO_3 solution (5%, 1 L), and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with aq. $NaHCO_3$ solution (5%, 150 mL), dried, and carefully concentrated by use of a 30 cm rectification column under ambient pressure (bath temperature < 55°C) to give crude basketenes **8b** and **8c** of rather high purity. They can additionally be purified by column chromatography on silica gel, with elution with dichloromethane, but the yield drops after purification.

4-(Trimethylsilyl)pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene (4-trimethylsilylbasketene, 8b): Basketene **8b** (crude: 3.20 g, 46%; purified: 1.70 g, 25%) was obtained from diacid **7b** (10.0 g, 34.2 mmol) and $Pb(OAc)_4$ (30.0 g, 67.7 mmol) according to GP 4, as a colorless oil. ^{1}H NMR (270 MHz, C_6D_6): δ = 6.55 (m, 2H; 2=CH), 3.67 (m, 1H; CH), 3.51 (m, 1H; CH), 3.12 (m, 1H; CH), 2.66 (m, 2H; 2CH), 2.57 (m, 2H; 2CH), 0.02 ppm (s, 9H; 3CH_3); IR (film): $\tilde{\nu}$ = 3050, 2950, 1240, 830 cm^{-1}; MS (EI): *m*/*z* (%): 202 (5) $[M]^+$, 187 (10) $[M - Me]^+$, 159 (31), 129 (51) $[M - SiMe_3]^+$, 128 (40), 109 (100); elemental analysis calcd (%) for $C_{13}H_{18}Si$ (202.4): C 77.16, H 8.96; found C 76.86, H 8.57.

4-Acetoxymethylpentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene (4-acetoxymethylbasketene, 8c): Basketene **8c** (crude: 2.40 g, 50%; purified: 2.10 g, 43%) was prepared from diacid **7c** (7.0 g, 23.9 mmol) and $Pb(OAc)_4$ (22.50 g, 50.7 mmol) according to GP 4, as a colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.50 (m, 2H; 2=CH), 4.20 (s, 2H; OCH_2), 3.60–3.80 (m, 2H; 2CH), 3.20 (m, 1H; CH), 2.70–2.50 (m, 4H; 4CH), 2.10 ppm (s, 3H; CH_3); MS (EI): *m*/*z* (%): 202 (7) $[M]^+$, 143 (41), 142 (100) $[M - HCO_2Me]^+$, 141 (72) $[M - HCO_2Me - H]^+$, 129 (31), 128 (40), 115 (53), 91 (89); elemental analysis calcd (%) for $C_{13}H_{14}O_2$ (202.2): C 77.20, H 6.98; found C 69.93, H 7.02.

Preparation of 4-substituted pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-enes (snoutenes) 9a and 9b

General procedure GP 5: Silver nitrate (150 mg) was added to a solution of the appropriate basketene **8** (10 mmol) in anhydrous methanol (100 mL), and the resulting solution was stirred at 50°C under argon for 48 h with TLC monitoring (eluent dichloromethane). After the mixture had cooled, the solvent was removed under reduced pressure, and the residue was diluted with water (100 mL) and extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried and carefully concentrated by use of a 30 cm rectification column under ambient pressure. The product was purified by column chromatography of the residue on silica gel, with elution with CH_2Cl_2.

4-(Trimethylsilyl)pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (4-trimethylsilylsnoutene, 9b): Snoutene **9b** (1.28 g, 85%) was prepared from basketene **8b** (1.50 g, 7.4 mmol) according to GP 5, as a colorless oil, which solidified upon standing at 0°C. Mp. 56°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.50–6.40 (m, 2H; 2=CH), 3.13 (m, 2H; 2CH), 2.00 (t, *J* = 7.0 Hz, 1H; CH), 1.70–1.60 (m, 4H; 4CH), 0.10 (s, 9H; 3CH_3) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 131.7, 131.5 (CH), 41.5, 39.6, 39.5 (2CH), 38.6 (CH), 38.4 (C), –3.1 ppm (3CH_3); IR (film): $\tilde{\nu}$ = 3050, 3010, 2950, 1240, 830 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{18}Si$ (202.4): C 77.16, H 8.96; found C 76.56, H 8.77.

4-Acetoxymethylpentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (4-acetoxymethylsnoutene, 9c): Snoutene **9c** (1.70 g, 85%) was prepared from basketene **8c** (2.0 g, 9.9 mmol) according to GP 5, as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.40 (m, 2H; 2=CH), 4.25 (s, 2H; OCH_2), 3.30–3.20 (m, 3H; 3CH), 2.10 (s, 3H; CH_3), 1.60 (m, 4H; 4CH); MS (EI): *m*/*z* (%): 202 (5) $[M]^+$, 159 (18) $[M - COMe]^+$, 143 (38), 142 (100) $[M - HCO_2Me]^+$, 141 (70) $[M - HCO_2Me - H]^+$, 129 (35), 128 (43), 115 (50), 91 (78).

4-Trimethylsilyloxymethylpentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (4-(trimethylsilyloxymethyl)snoutene, 9d): Snoutene **9c** (1.50 g, 7.4 mmol) was stirred in aq. NaOH solution (10%, 10 mL) at ambient temperature with TLC monitoring (eluent dichloromethane). After complete disappearance of the starting material (ca. 3 h), the reaction mixture was poured into water (50 mL) and extracted with Et_2O (10 × 25 mL). The combined organic extracts were dried and concentrated under reduced pressure to give essentially pure 4-hydroxymethylpentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (4-hydroxymethylsnoutene, 1.11 g, 6.93 mmol, 94%), which was immediately taken up with anhydrous dichloromethane (10 mL) and stirred with trimethylsilyl chloride (760 mg, 7 mmol) and triethylamine (708 mg, 7 mmol) at ambient temperature for 2 h. The reaction mixture was concentrated under reduced pressure, and the residue was taken up with Et_2O (30 mL), washed with water and brine (10 mL each), dried, and concentrated again to give snoutene **9d** (1.39 g, 81% over two steps) as a colorless oil, which was used in the next step without further purification. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.40 (m, 2H; 2=CH), 4.20 (s, 2H; OCH_2), 3.20 (m, 3H; 3CH), 1.60 (m, 4H; 4CH), 0.10 ppm (s, 9H; 3CH_3).

Preparation of 6- and 1-substituted hexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decanes (diademanes) 1b, 1e, 1f, and 10b

General procedure GP 6: A solution of the appropriate snoutene (3–8 mmol) in anhydrous olefin-free pentane (1.5 L) was irradiated under nitrogen with a 450 W medium-pressure mercury lamp (Hanovia 6515–34) in a quartz reactor at –65°C under an atmosphere of argon, with monitoring of the conversion by ^{1}H HMR spectroscopy. The irradiation was stopped when the proportion of starting material to product was approximately 60:40 (ca. 72 h). The reaction mixture was concentrated under reduced pressure and, if not otherwise specified, the residue was taken up with Et_2O (10 mL), quickly filtered through a short pad of silica gel at –25°C, and concentrated again. The residue was taken up with dichloromethane (20 mL) and treated with *m*-CPBA in 50 mg portions at 0°C until the starting material had been completely consumed (GC monitoring). The reaction mixture was concentrated under reduced pressure and the residue was separated by column chromatography on silica gel at –25°C (eluent pentane/Et_2O 10:1).

6-(Trimethylsilyl)hexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane (6-trimethylsilyldiademane, 1b) and 1-(trimethylsilyl)hexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane (1-trimethylsilyl-diademane, 10b): From the snoutene **9b** (750 mg, 3.7 mmol), an inseparable 3:1 mixture of **1b** and **10b** (231 mg, 31%) was obtained according to GP 6, as a colorless solid. **1b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.60–2.55 (m, 3H; 3CH), 1.65–1.50 (m, 6H; 6CH), 0.15 ppm (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 56.8 (3CH), 23.6 (6CH), 0.3 (C), –2.0 ppm (3CH_3). **10b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.80 (m, 2H; 2CH), 2.40 (t, *J* = 7.0 Hz, 1H; CH), 1.45–1.20 (m, 6H; 6CH), 0.05 ppm (s, 9H; 3CH_3). Attempted preparative GC separation of **1b** and **10b** led to their complete isomerization into a mixture of trimethylsilyl-substituted triquinacenes **3b** and **11b**.

10-(Trimethylsilyl)tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (10-trimethylsilyltriquinacene, 3b): ^{1}H NMR (270 MHz, C_6D_6): δ = 5.52 (s, 6H; 6=CH), 3.42 (s, 3H; 3CH), –0.02 ppm (s, 9H; 3CH_3); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 133.0 (6CH), 60.6 (3CH), 45.3 (C), –5.5 ppm (3CH_3).

6-Hydroxymethylhexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane (6-hydroxymethyldiademane, 1e): Snoutene **9d** (750 mg, 3.23 mmol) was treated according to GP 6 to give 6-(trimethylsilyloxymethyl)hexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]-decane [1-(trimethylsilyloxymethyl)diademane, **1d**] (33.9 mg, 4.5%) as a colorless solid. This was taken up with anhydrous THF (1 mL) and stirred with nBu_4NF (0.15 mmol, 0.15 mL of a 1M solution in THF) at ambient temperature for 15 min. The reaction mixture was concentrated under reduced pressure, and the product was then purified by flash column chromatography on silica gel at –25°C (eluent pentane/Et_2O 10:1). Diademane **1e** (15 mg, 2.9% over two steps) was obtained as a colorless solid. M.p. 104–110°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.80 (d, *J* = 6.0 Hz, 2H; OCH_2), 2.80–2.60 (m, 3H; 3CH), 1.65 ppm (d, *J* = 6.0 Hz; 6H, 6CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 67.2 (CH_2), 63.6 (C), 54.4 (3CH), 21.0 ppm (6CH).

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6-Methylhexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane (6-methyldiademane, 1 f): Snoutene **9 f**[10] (360 mg, 2.50 mmol) was irradiated according to GP 6, but with use of a falling-film reactor.[32] After evaporation of the pentane, the mixture was separated by preparative gas chromatography to give an 8:1 mixture of 10- and 1-methyltricyclo[5.2.1.0^{4,10}]deca-2,5,8-trienes (10- and 1-methyltriquinacenes **3 f** and **11 f**, 22 mg, 6%), the starting material **9 f** (180 mg, 50%), and 1-methyldiademane (**1 f**, 60 mg, 17%) as a colorless oil.

Compound 3 f: ^{1}H NMR (270 MHz, C_6D_6): $\delta = 5.49$ (s, 6H; 6=CH), 3.09 (s, 3H; 3CH), 1.24 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 132.6$ (6CH), 65.5 (3CH), 57.5 (C), 26.6 ppm (CH_3).

Compound 11 f:[33] ^{1}H NMR (270 MHz, C_6D_6): $\delta = 5.50$ (s, 2H; 2=CH), 5.44 (s, 4H; 4=CH), 3.62 (d, $J = 8.8$ Hz, 2H; 2CH), 3.10 (t, $J = 8.8$ Hz, 1H; CH), 1.21 ppm (s, 3H; CH_3).

The mass spectra of hydrocarbons **3 f** and **11 f** were almost identical to those of the starting material **9 f** and to that reported for **11 f**.[33]

Compound 1 f: ^{1}H NMR (270 MHz, C_6D_6): $\delta = 2.46$ (t, $J = 7.2$ Hz, 3H; 3CH), 1.48 (d, $J = 7.2$ Hz, 6H; 6CH), 1.25 ppm (s, 3H; CH_3); MS (EI): *m*/*z* (%): 144 (7) $[M]^+$, 143 (10) $[M-H]^+$, 129 (100) $[M-Me]^+$, 103 (61), 77 (82).

The corresponding 1-methylhexacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}.0^{7,9}]decane (1-methyldiademane, **10 f**) was not detected among the products after GC separation.

Kinetics of the rearrangement of diademanes 1 b and 1 f in solution: NMR tubes were filled with 0.1M solutions of the appropriate diademane in [D_6] benzene, carefully degassed by three freeze-pump-thaw cycles, and then sealed. The tubes were immersed in a stirred silicone oil thermostat (temperatures were controlled in a range of $\pm 0.1\,^\circ$C). The tubes were taken out of the heating bath after the appropriate length of time, and the reaction was quenched by immersion of the tube in ice/water. The ratios of the products to starting materials were determined from their ^{1}H NMR spectra. The average values of four integrations were used in the ensuing calculations.

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270(2) K, $\rho_{calcd} = 1.121\ g\,cm^{-3}$, $\mu = 0.157\ mm^{-1}$, intensities measured: 1733 ($2\theta_{max} = 50.06^\circ$), independent: 1118 ($R_{int} = 0.0308$), 89 parameters refined, R indices (all data): $R_1 = 0.0554$, $wR_2 = 0.1405$, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0518$, $wR_2 = 0.1362$, Gof = 1.098, maximum and minimum residual electron density 0.212 and $-0.251\ e\,Å^{-3}$. **1e**: $C_{11}H_{12}O$ (160.21), crystal size $0.5 \times 0.5 \times 0.4$ mm, monoclinic, $a = 6.211(1)$, $b = 10.476(4)$, $c = 18.225(3)$ Å, $\alpha = \gamma = 90$, $\beta = 90.40(3)^\circ$, $V = 1185.8(5)$ Å^3, $Z = 6$, space group Pc, $T = 153(2)$ K, $\rho_{calcd} = 1.346\ g\,cm^{-3}$, $\mu = 0.084\ mm^{-1}$, intensities measured: 4763 ($2\theta_{max} = 55.0^\circ$), independent: 4753 ($R_{int} = 0.0096$), 337 parameters refined, R indices (all data): $R_1 = 0.0606$, $wR_2 = 0.1274$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0463$, $wR_2 = 0.1167$, Gof = 1.038, maximum and minimum residual electron density 0.263 and $-0.247\ e\,Å^{-3}$. CCDC-209471 (**9b**) and CCDC-208902 (**1e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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