DOI: 10.1002/ejoc.200700397

In Pursuit of *cis*,*cis*,*cis*-Cyclonona-2,5,8-triene-1,4,7-trione – An Adventure in Medium-Sized Ring Chemistry

Axel Pleschke,[a] Jens Geier,*[b][‡] Manfred Keller,[a] Jürgen Wörth,[a] Lothar Knothe,[a] and Horst Prinzbach*[a]

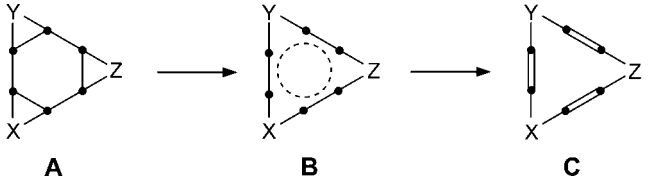
Dedicated to William von Eggers Doering on the occasion of his 90th birthday

Keywords: Tris σ/π-Homobenzenes / Cyclononanes, highly functionalized, bridged / Calculations

Attempts to synthesize the long soughtafter tris-π-homobenzene *cis*,*cis*,*cis*-2,5,8-cyclononatriene-1,4,7-trione, via the newly prepared cyclononane-1,4,7-trione ($C_9H_6O_3$), through base-catalysed threefold HBr elimination from an efficiently prepared and stereochemically uniform tribromo derivative, failed due to typical medium-ring complications, transannular reactions and an exceptional ease of polymerization. In the cations generated in the vapour phase through electron-impact ionization (MS), the threefold elimination of (H)Br, competing with the elimination of CO, led to $C_9H_7O_3^+$ ions, whereas the impressively neat anionic three-step fragmentation pathway resulted in $C_9H_6O_3^-$ ion(s). Whilst the compositions of these bromine-free ions, which were in part computationally approached {B3LYP/6-31+G(d,p)}, and their assignments appeared compatible with the protonated and anionic target molecules, their true natures remain open. X-ray structural analyses for several (bridged) nine-membered ring compounds are provided.

Introduction

cis-Tris-σ-homobenzenes **A**, containing three three-membered rings annulated to the face of a planar six-membered ring, originally attracted attention as highly strained structural peculiarities and in particular as mechanistic probes. Their thermal transformations into the corresponding cyclononatrienes **C** constituted highly topical, unprecedented [σ2s + σ2s + σ2s] cycloreversion reactions – consisting of concerted scissions of three C–C bonds via trishomobenzenoid transition states **B**.[1,2] Broad variation of the X,Y,Z-structural elements not only helped to establish the prerequisites of this mechanism and to quantify its energetic advantage, but also allowed multifaceted applications in synthesis (see Concluding Remarks).



Long missing members in this now large ballpark of σ/π-trishomobenzenoid systems were the triketones **A** and **C** (X,Y,Z = C=O): the "triscyclopropanone" **1** and the *cis*,*cis*,*cis*-cyclononatrienetrione **2**. According to recent calculations (Figure 1)[3–9] **1** is indeed C_{3v}-symmetrical with a perfectly planar six-membered ring and dihedral angles of 113.6° formed with the three-membered rings. For comparison, the *trans* isomer **3** (Figure 1) is as expected lower in energy by 11.6 kcal mol^{-1}, due mainly to reduced transannular repulsion and H/H strain, and the dihedral angles are 112.4 and 111.3°. With an expected activation barrier for the isomerization **1** → **2** somewhere between that of the hydrocarbon **A** (X,Y,Z = CH_2, $E_a \approx 22$ kcal mol^{-1}) and that of trioxide **A** (X,Y,Z = O, $E_a \approx 40$ kcal mol^{-1}), this route to the presumably highly reactive triene **2** looked very promising. For **2**, as for its trismethylene derivative (**4**) and many of the heteronines **C**, the C_{3v} conformation (**2a**) is not a minimum, but rather corresponds to a second-order saddle point. The most stable form is the C_2-symmetrical **2c**, which possibly interconverts via the C_s-symmetrical saddle **2b** (higher in energy by 2.4 kcal mol^{-1} [3]).

[a] Chemisches Laboratorium der Universität Freiburg i. Br., Institut für Organische Chemie und Biochemie,
Albertstr. 21, 79104 Freiburg i. Br., Germany
Fax: +49-761-203-6048
E-mail: horst.prinzbach@orgmail.chemie.uni-freiburg.de
[b] Bergische Universität Wuppertal, FB C-Anorganische Chemie
Gaußstr. 20, 42097 Wuppertal
E-mail: geier@uni-wuppertal.de
[‡] Present address: Chemisches Laboratorium der Universität Freiburg i. Br., Institut für Organische Chemie und Biochemie, Albertstr. 21, 79104 Freiburg i. Br., Germany.
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

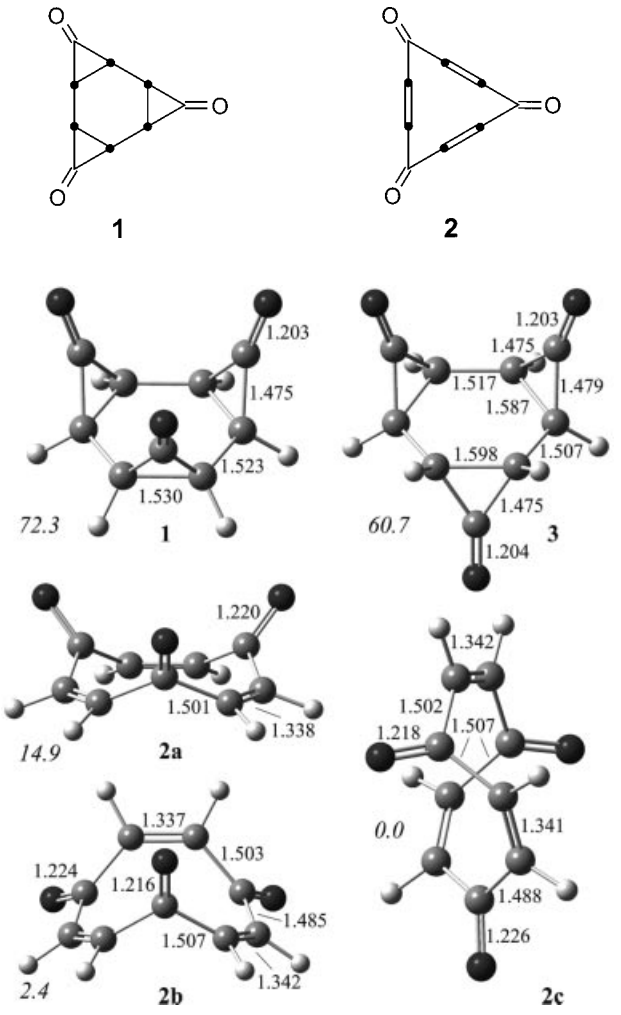
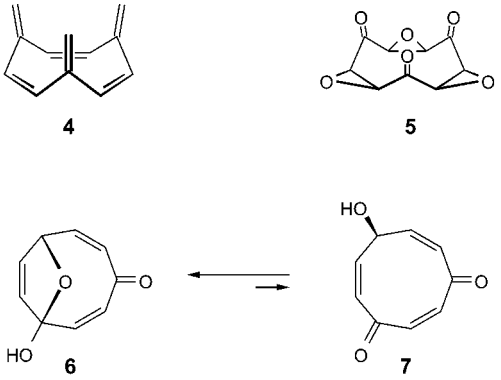
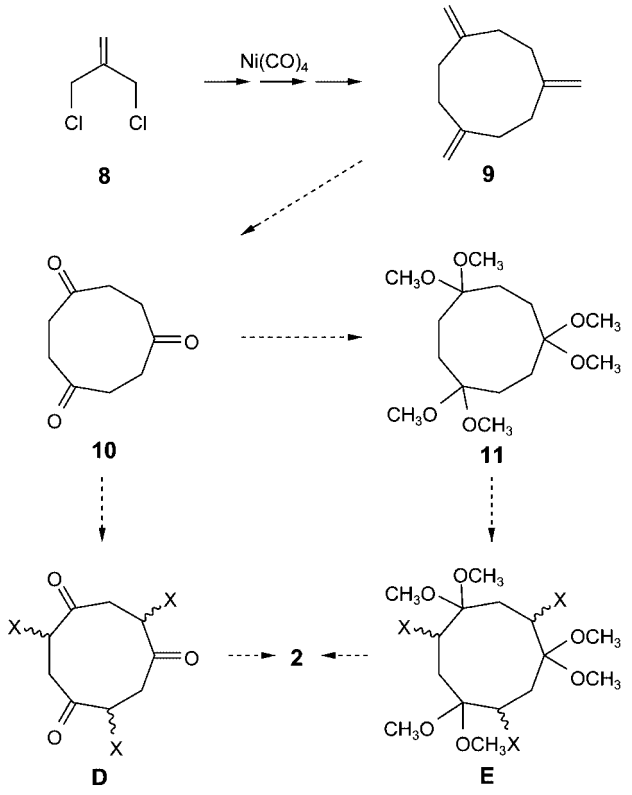


Figure 1. Calculated structures of **1**, **2a**–**c** and **3** {B3LYP/6-31+G(d,p); distances in Å, *relative energies* in kcal mol^{-1}}.

Efforts to prepare **1** starting from carbocyclic, kinetically rather labile precursor molecules **A** with X,Y,Z = $CHCO_2CH_3$ or CHCN[10] were limited by the anticipated amount of time needed for the latter's preparation and were finally stopped. Already described in detail are our ultimately fruitless attempts to synthesize **2** starting from the triester **A** (X,Y,Z = $CHCO_2CH_3$) or the commercially available 1,5-cyclooctadiene.[11] The trismethylenetriene **4** and the trisepoxytrione **5** were prominent intermediates on these routes. With the bicyclic hemiacetal **6** we had come close to **2**, yet ultimately failed to attain it, when no means were found to effect, after equilibration, the oxidation of the hydroxy diketone **7** (calculated[3] to be 2.3 kcal mol^{-1} less stable than **6**).

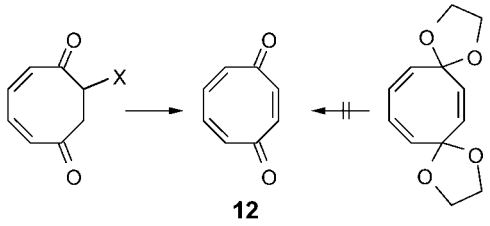


In a final contribution to this topic, here we detail attempts to prepare **2** starting from 1,4,7-trismethylenecyclononane (**9**) via the then surprisingly still unknown cyclononane-1,4,7-trione (**10**)[12] and its trisacetal **11**, through threefold α-functionalization (**D**, **E**) followed by threefold β-HX elimination (Scheme 1).[13–15]



Scheme 1.

The prospects and risks of this endeavour had been highlighted in the experience gathered by the groups of Kitahara and Raphael in their early attempts to synthesize the structurally very similar cycloocta-2,5,7-triene-1,4-dione (**12**), which could be secured in modest yield through a final β-HBr elimination reaction,[16] but not, however, through cleavage of its bisethylene acetal.[17] It was also clear that transannular bond formation would be an omnipresent complication with such nine-membered rings. In fact, such

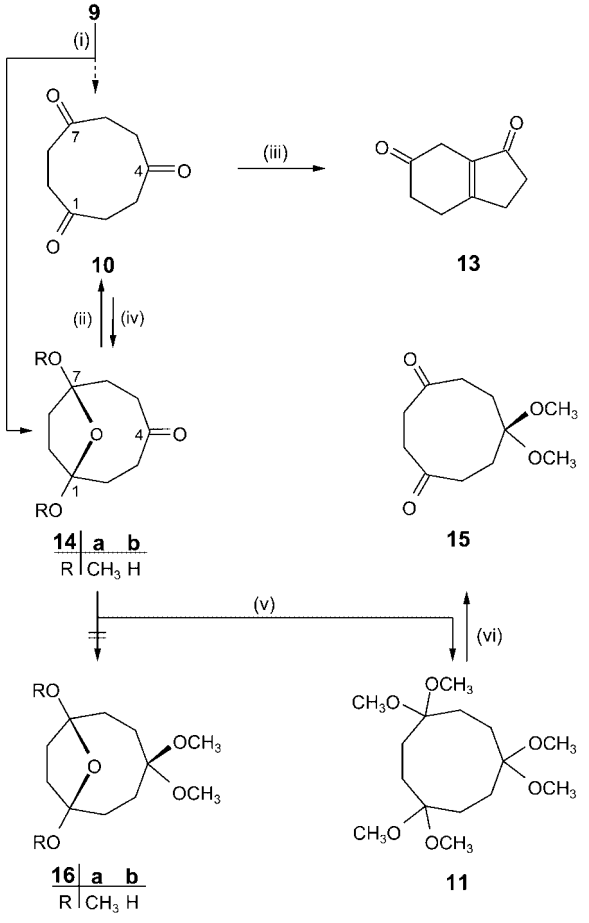


interfering events had previously even prevented the synthesis of triply benzoanellated derivatives of **2** (cyclotriveratrylenetriones).[18]

Results and Discussion

Cyclononane-1,4,7-trione (10)

For a one-pot oxidative cleavage of the three C=C double bonds of the C_{3v}-symmetrical **9** (NMR), notwithstanding the aspect of complicating transannular reactions, ozonization seemed to be the most promising approach (Scheme 2). However, after treatment of **9** in CH_2Cl_2 with O_3 at –78 °C until total conversion, followed by reduction with dimethylsulfide, trione **10** was detectable, if at all, only as a very minor component in a very complex product mixture. With CH_3OH as a "participating solvent", however, the situation changed dramatically. After an appropriately short isolation procedure, a crystalline, C_s-symmetrical product was isolated in nearly quantitative yield. According to its elemental composition a dimethyl acetal of **10** had been formed, and was identified as the bicyclic **14a** rather than the monocyclic **15**. That **14a** did not react further to give **16a** is understandable in view of the reduced electrophilic character of the carbonyl group – the calculated O↔CO distance in its low-energy conformation is 2.668 Å (Figure 2) – and the implied costs in steric strain.



Scheme 2. i) $O_3/CH_2Cl_2,CH_3OH$/–78 °C. CH_3SCH_3/room temp./86%. ii) CH_3COCH_3, H^+/40 °C/2 h/repet./95%. iii) CH_3CN,H_2O (1:1), 2 N HCl/4 h/room temp./81%. iv) $CH_3COCH_3/H_2O(H^+)$. v) TMSOTf/CH_3OH/–70 °C → –20 °C/15 min/84%. vi) CH_3COCH_3/H_2O (trace H^+).

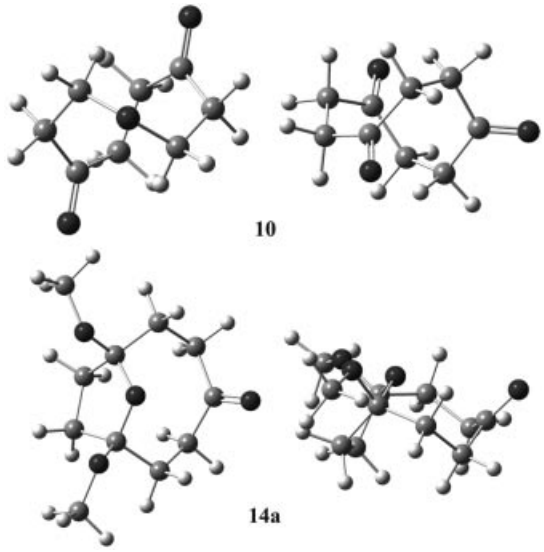


Figure 2. Calculated {B3LYP/6-31+G(d,p)[3]} low-energy conformations of **10** and **14a**.

The product isolated from **14a** in 84% yield upon strong electrophilic activation with a TMSOTF/CH_3OH combination at low temperature (–78 → –20 °C) was indeed not **16a** but the trisdimethyl acetal **11**. This, like 1,1,4,4,7,7-hexamethylcyclononane,[19] prefers a D_3-symmetrical twisted chair-boat conformation {three ^1H and ^{13}C NMR signals, T_{coalsc} ([D$_6$]DMSO) = 55 °C, E_a = 19 kcal mol^{-1}} both in solution and in the solid state. Crystals of **11** suitable for structural analysis[20] were obtained from a dry 1:1:1 acetone/diethyl ether/cyclohexane mixture. Crystals of the dimethyl acetal **15** were serendipitously isolated from a solution of **11** in acetone not protected from moisture.

For the conversion of **14a** into the highly acid-sensitive **10**, various standard alternatives were tested. A somewhat time-consuming, discontinuous transacetalization procedure with acetone and catalytic amounts of sulfosalicylic acid turned out to be the best choice. After equilibration and concentration, the procedure was repeated until **10** was quantitatively liberated. Before the final concentration, the acid has to be carefully neutralized to avoid intramolecular condensation of **10** into the bicyclic **13**. Use of 1,1-difluoroacetone or chloral instead of acetone increased the equilibrium amount of **10** only to 20–25% and hence brought no decisive advantage. In aqueous acetone containing a trace of acid, **10** equilibrated with the hydrate **14b** (no sign of **16b**), which, however, reverted to **10** during the isolation procedure. For the colourless, crystalline **10**, the ^1H (one line, δ = 2.62 ppm) and ^{13}C NMR spectra (two lines, δ = 210.5, 39.6 ppm), taken at 25 °C in $CDCl_3$ solutions, established averaged C_{3h} symmetry (cf. **9**). In the C_2-symmetrical

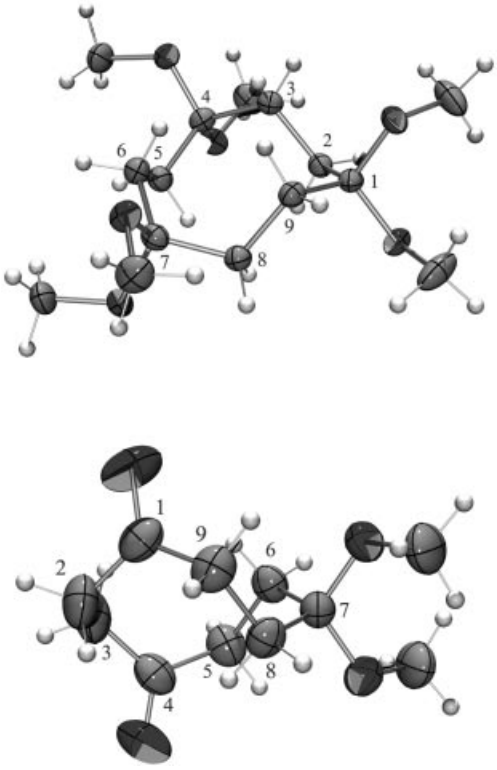
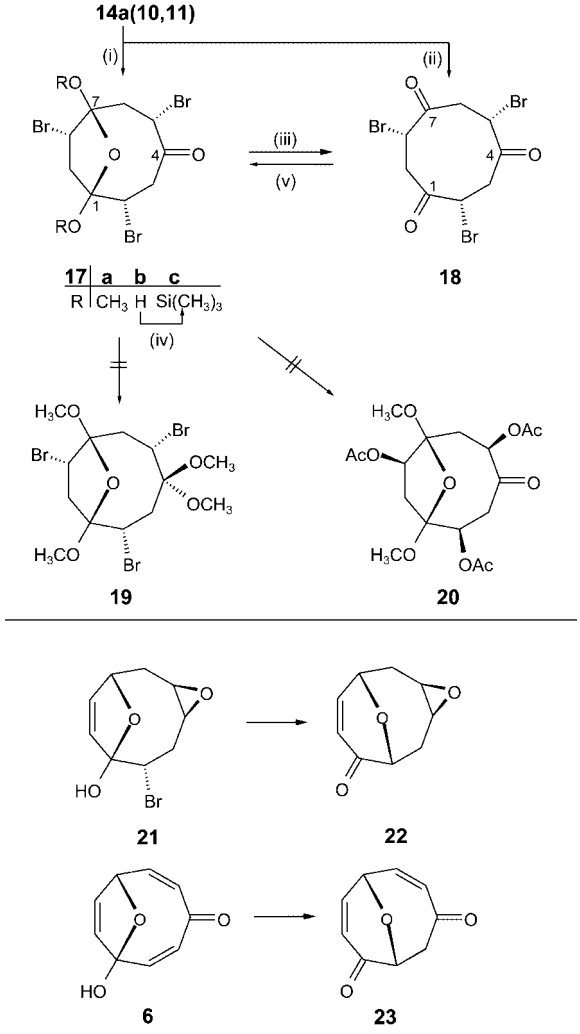


Figure 3. ORTEP plots of the X-ray structures of **11** (100 K) and **15** (room temp.).

low-energy conformation (Figure 2) the relative orientation of the carbonyl groups obviously invites transannular bridging upon nucleophilic attack.

Precursors of 2

With trione **10** and its acetals **11** and **14a** to hand, the first attempts directed at the trienetrione **2** concentrated on threefold β-elimination in the tribromides of type **D** and **E** (Scheme 1, X = Br).[16] Explorative bromination experiments in nonparticipating solvents (Br_2/CH_2Cl_2 or $PyHBr_3$/THF[21]) generally led after total conversion (^1H NMR, MS) to reaction mixtures containing α-bromo ketones and α-bromo acetals, respectively, but were too complex to allow any separation. Once again (Scheme 3), participating methanol as solvent made the difference. Treatment of **14a** with three equivalents of $PyHBr_3$ delivered the bicyclic 2β,5β,8β-tribromide **17a** in nearly quantitative yield (83–80% when starting from **10** or **11**). An intensive search for intermediates or isomers with differing substitution patterns, to gain some insight into the transformations **14a** (**10**, **11**) → **17a**, was not successful. Even with greatly reduced amounts of reagent, **17a** remained the only observed product, an indication that the three bromination steps proceed with increasing rates. The situation changed with the use of *t*BuOH as solvent: after treatment with 3.3 equiv. of $PyHBr_3$ at 3 °C the monocyclic 2β,5β,8β-tribromo-1,4,7-trione **18** was the main product together with several small, unidentified components, but could not be isolated in pure form, due to its extreme tendency to add water. Upon chromatography of crude **18** on silica gel, bicyclic **17b** was obtained in 85% yield. Unlike **14b**, and in line with a high, bromine-mediated stability, this compound did not lose water to give **18** when heated as mixture with P_2O_5 at 10^{-4} Torr. An expeditious route to **18** was opened up when treatment of **17a** with boron tribromide (BBr_3) under strictly anhydrous conditions allowed not only a rapid and neat deacetalization but also a necessarily rapid isolation procedure. After stirring of a dilute benzene solution of **17a** and ca. 3 equivalents of BBr_3 at 3 °C until total conversion (TLC), followed by concentration and extraction of the solid residue with cyclohexane and drying at 10^{-4} Torr, the pale yellow, crystalline tribromotrione **18** was obtained nearly quantitatively. Three ^1H and ^{13}C signals in the NMR spectra [^1H: δ = 4.05 (dd, 2-,5-,8-H), 2.69 (dd, 3-,6-,9-H_{endo}), 2.10 (dd, 3-,6-,9-H_{exo}); $J_{2,3endo}$ = 12.5, $J_{2,3exo}$ = 5.8, $J_{3endo,3exo}$ = 14.9 Hz. ^{13}C: δ = 196.3 (C-1,-4,-7), 48.9 (C-2,-5,-8), 39.2 (C-3,-6,-9)] confirmed averaged C_3 symmetry. The calculated low-energy conformation (Figure 4), much



Scheme 3. i) $CH_3OH/PyHBr_3$/room temp./6 h/90–95%. ii) *t*BuOH/$PyHBr_3$/room temp./5 h/85%. iii) BBr_3/benzene/3 °C/5 h/93%. iv) $TMSCN/CH_2Cl_2$/reflux/14 h/89%. v) SiO_2/85%.

like that of trione **10** (Figure 2), showed C=O groups ideally set up for transannular bridging (distance between *cis*-oriented carbonyl C atoms = 3.039 Å).

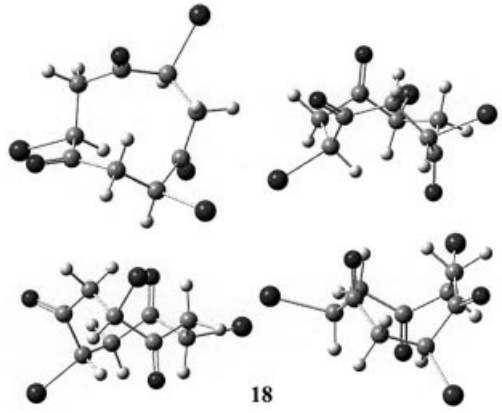


Figure 4. Different views of the calculated {B3LYP/6-31+G(d,p)[3]} low-energy conformation of tribromotrione **18**.

The stereochemical details of **17a** as based on the ^{1}H and ^{13}C NMR spectra could be confirmed by an X-ray structural analysis (Figure 5, Table 1).[20] The O↔CO distance of 2.554 Å is slightly shorter than the calculated value of 2.668 Å in **14a**. There is a fairly good agreement of measured H,H dihedral angles with those derived from the ^3J(H,H) NMR coupling constants (Karplus equation[22]), which demonstrates fairly similar conformational situations in the solid state and in solution. The solid-state Br,H dihedral angles are all of such a value as to make E_2 β-HBr eliminations rather difficult, thus possibly promoting polymerization of the, compared with **18**, rather rigid bicyclic skeletons. It is clear that further bromination in **17a**, as well as acetalization to give **19** (cf. **16**), would face strong steric inhibition. Not too surprising was the failure to effect S_N2- or S_N1-type nucleophilic substitutions in **17a** to give, for example, the 2α,5α,8α-trishydroxyacetate **20** as a much desired alternative precursor molecule of **2** (through vapour-phase pyrolysis). Compound **17a** thus survived forcing treatment with NaN_3/DMF at 90 °C and with NaN_3/Ag-O_2CCF_3/H_2O at 100 °C. Under even more forcing conditions an apparently olefinic product slowly appeared (^{1}H NMR, **24a**, Scheme 5).

With the "trienetrione hydrate" **26b** (Scheme 5), of interest as an alternative precursor for targeting of **2**, bistrialkylsilylation of **17b** was pursued as a protecting measure in the hope that deprotection of **26c** could possibly be achievable under conditions more suitable for the target molecule. When **17b** (pK_a ca. 13) was exposed to standard trimethylsilylation methods, however, either no reaction (TMSCl or $TMSSO_2CF_3$/imidazole/DMAP/DMF;[23] TMS/Li_2S/CH_3-CN[24]) or rapid decomposition (with triethylamine instead of imidazole as base) to a brownish-black, viscous material

Table 1. Bond lengths, bond angles, and selected NMR data.

17a					
C4–O	1.214(4)	C1–C2–C3	113.1(3)	C2–C3–C4	108.5(3)
C2–Br	1.958(3)	C3–C4–C5	119.4(3)	C4–C5–C6	116.9(3)
C5–Br	1.971(3)	C5–C6–C7	112.3(2)	C6–C7–C8	114.2(3)
C8–Br	1.952(2)	C7–C8–C9	103.6(2)	C8–C9–C1	108.5(3)
24a					
C4–O:	1.214(3)	C1–C2–C3	125.7(2)	C2–C3–C4	126.7(2)
C5–Br	1.978(2)	C3–C4–C5	119.1(2)	C4–C5–C6	117.5(2)
C8–Br	1.951(2)	C5–C6–C7	111.4(2)	C6–C7–C8	114.0(2)
C2–C3	1.328(4)	C7–C8–C9	103.5(2)	C8–C9–C1	102.8(2)
26a					
C4–O	1.2187(17)	C1–C2–C3	124.40(13)	C2–C3–C4	128.47(13)
C2–C3	1.318(2)	C3–C4–C5	121.82(12)	C4–C5–C6	128.04(13)
C5–C6	1.316(2)	C5–C6–C7	124.35(13)	C6–C7–C8	112.11(12)
C8–C9	1.298(2)	C7–C8–C9	110.96(14)	C8–C9–C1	110.14(13)
17a					
	^3J	H/H(NMR)	H/H	Br/H	
2,3α	4.5	65–75	69.8	BrH3α	47.9
2,3β	12.3	165–175	170.9	BrH3β	71.4
5,6α	8	50–60	54.5	BrH6α	64.4
5,6β	11.5	160–175	172.2	BrH6β	53.2
8,9α	5	35–45	40.0	BrH9α	81.6
8,9β	12.3	160–170	162.4	BrH9β	40.8
24a					
	^3J	H/H(NMR)	H/H	Br/H	
5,6α	4.3	40–50	53.8	BrH6α	53.4
5,6β	12.5	160–170	171.8	BrH6β	64.7
8,9α	9.3	140–150	155.5	BrH9α	87.9
8,9β	10.7	15–25	33.7	BrH9β	33.9

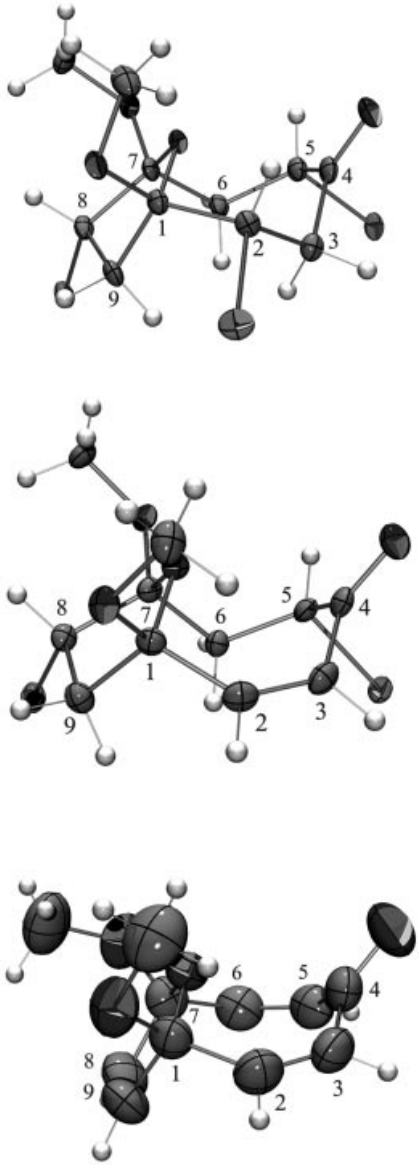
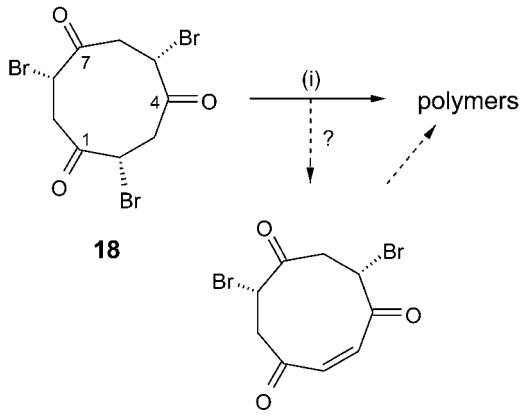


Figure 5. ORTEP plots of the X-ray structures of **17a** (100 K), **24a** (100 K) and **26a** (r.t.); selected bond lengths (Å) and bond angles (°). For **17a** and **24a**, ^3J(H/H) coupling constants (Hz), calculated (H/H, NMR) and experimentally determined (X-ray) dihedral H/H and Br/H angles (°).

containing halogen, OH– and C=O groups (IR) occurred. Application of TMSCN/CH_2Cl_2[25] in large excess solved the problem. After heating at reflux for 14 h and filtration through deactivated silica gel, an 89% yield of neat **17c** was isolated. Indications of the reaction complexity in the response of **17b** towards even comparably weak bases have been reported in a preceding study:[11] the structurally close **21** had been transformed in boiling DBN/toluene, inter alia, into **22**, and **6** had been isomerized under Oppenauer conditions into **23**.

Triple HBr Eliminations

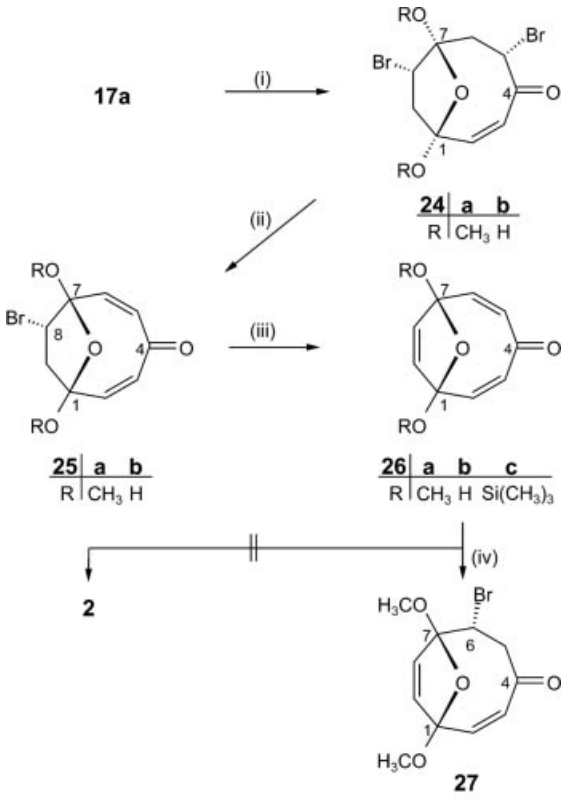
The base-catalysed triple β-elimination of HBr from the tribromotrione **18** as a potential route to **2** (Scheme 4) was a priori problematic, by whatever mechanism. For E_2 eliminations, the given conformational situations are highly unfavourable: the carbanions generated along E1cb routes, whilst reluctant to expel β-Br anions, are prone, like trione **10**, to undergo kinetically and thermodynamically favourable transannular and intermolecular reactions. And indeed, in a series of experiments performed in aprotic, rigorously dried solvents with **18** and varying equivalents of weakly nucleophilic bases of differing strength and steric demand [inter alia $N(C_2H_5)_3$ (cf. **12**), DBU,[16] *t*BuOK, *t*BuP1,[26] P_2F[27]], between +5° and –78 °C, instant deposition of a bromine-containing, brownish-black polymer was noted, this being similar (IR) to the one observed for the attempted base-catalysed silylation of **17b**, and not amenable to NMR analysis. There was therefore no indication of any significant formation of olefinic products. In fact, given the ease of polymerization, β-elimination might not have occurred at all.

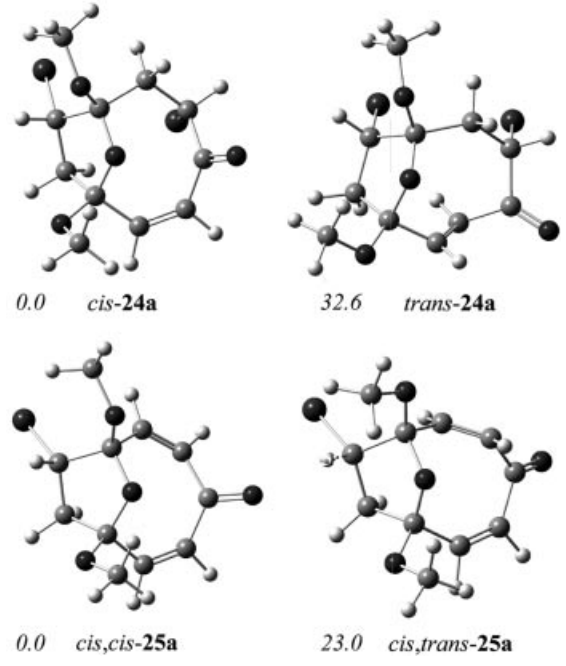


Scheme 4.i) i.a. $N(C_2H_5)_3$, DBU, *t*BuOK, *t*BuP1, P_2F (+5 °C → –78 °C).

With bicyclic **17a**, in contrast, no complications were encountered (Scheme 5). Unlike in the case of **18** there was no conversion after a toluene solution of **17a** had been kept with 10 equivalents of DBU at room temperature for 12 hours. After 2 hours at 50 °C, however, a nearly homogeneous product had been formed (TLC) and was chromatographically separated into the *cis*-monoene **24a** (82%, $J_{2,3}$ = 11.2 Hz) and the *cis,cis*-diene **25a** (3%, $J_{2,3}$ = 11.4, $J_{5,6}$ = 11.2 Hz). With 25 equivalents of base at 50 °C and 6 h reaction time, this ratio changed to ca. 1:2.5, a 25% yield of **24a** and a 61% yield of **25a** being isolated chromatographically. After the toluene solution had been heated at reflux with 40 equivalents of base for 12 h, only **26a** remained (TLC, ^{1}H NMR, 85–90% isolated; $J_{2,3}$ = $J_{5,6}$ = 11.3 Hz, C_s). As to the selective formation of the *cis*/*cis*,*cis* structures **24** and **25**, it is noted that the *trans*/*cis*,*trans* isomers were calculated[3] to be less stable by 32.6 and 23.0 kcal mol^{-1}, respectively.

The conformational subtleties are once more in fairly good agreement with the X-ray analyses of **24a** and **26a** (Figure 5).[20] With O↔CO distances of 2.5536 and 2.55 Å, the enone subunits depart from planarity by 71.3° and



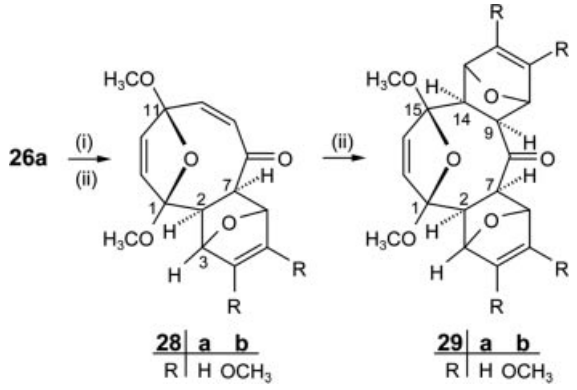


Scheme 5. i) Toluene/10 equiv. of DBU/50 °C/2 h. ii) Toluene/25 equiv. of DBU/80 °C/5 h. iii) Toluene/40 equiv. of DBU/reflux/12 h. iv) Bromocatecholborane/CH_2Cl_2/room temp./4 h. Calculated[3] structures of **24a** and **25a** and of the corresponding *trans*/*cis*,*trans* isomers (*relative energies* in kcal mol^{-1}).

68.6°, respectively, as expressed in $\tilde{\nu}_{C=O}$ frequencies (1706 and 1701 cm^{-1}, respectively) and $\pi\rightarrow\pi^*$/$n\rightarrow\pi^*$ UV absorptions {CH_3CN, 199 nm (ε = 10280)/290 nm (70); 200 nm (ε = 11200), 229 (sh, 985)/314 nm (20), respectively}.

The deacetalization of **26a** (→ **2**) was expected to be even more problematic than that of the saturated **11** (→ **10**) and **17a** (→ **18**). In fact, experiments with a series of protic and Lewis acids and even with the mild transacetalization (acetone) and deacetalization (BBr_3) procedures successfully applied to **11** and **17a** failed, producing instead a multitude of products and polymers (NMR, MS). ^{1}H NMR monitoring in CF_3CO_2H/$(CF_3CO)_2O$ gave no evidence of the intermediacy of **2** or of any defined protonated species. With bromocatecholborane as "tamed" BBr_3,[28] **26a** reacted selectively to give the 6β-bromide **27**, an isomer of **25a**. Vapour-phase dehydration of the trienone hydrate **26b** as an alternative route to the acid- and base-sensitive **2** had to be abandoned when directed dehydrobromination failed due to the base-sensitivity of **17b**. Similarly, the bistrimethylsilyl ether **17c**, when exposed to the weakly nucleophilic bases applied to **17b** and **18**, immediately formed insoluble polymers, even at –30 °C.

With interest in derivatives of **26a**, with the enone units protected for deacetalization by cycloaddition and then amenable to vapour-phase thermal [4+2]-cycloreversion, the response of **26a** towards 1,3-dienes was explored. Of several 1,3-dienes examined, only furans (Scheme 6) were successfully added, and then only under highly forcing high-pressure conditions (12 kbar/60 °C, at which polymerization of the diene is still avoided). After 12 days, a ca. 15% yield of monoadduct **28a** had been produced, together with trace amounts (< 1%) of, presumably, bisadduct **29a** (MS).[29] During chromatographic separation on silica gel a portion of **28a** underwent cycloreversion, while **29a** disappeared completely. With the more reactive 3,4-dimethoxyfuran at 14 kbar/25 °C after 11 days and ca. 30% conversion, ca. 20% of a ca. 4:1 mixture of **28b** and **29b** were chromatographically isolated and spectroscopically analysed as such (^{1}H, ^{13}C NMR, MS). The high tendency towards cycloreversion on silica gel made separation impossible. For **29a** and **29b**, C_s symmetry is established, the stereochemistry shown being based, with some reservations, on $J_{2,3}$ = 4.5, $J_{2,7}$ = 10.5 Hz for **28a** and 1.7 and 9.3 Hz for **28b**.



Scheme 6. i) Diethyl ether/furan/12 kbar/60 °C/12 d/11% **28a**. ii) Diethyl ether/3,4-dimethoxyfuran/15 kbar/room temp./11 d/26% **28b**/**29b** (4:1).

MS Fragmentation Patterns

For bicyclic tribromide **17a** ($C_{11}H_{15}Br_3O_4$) the 70 eV MS spectrum reveals two major elimination cascades beginning with $[M - (H)Br]^+$ and $[M - OCH_3]^+$, respectively, and producing as bromine-free ions fairly intense *m/z* = 211 (21) and *m/z* = 179 (40) fragments that were confirmed through high-resolution (HR) measurements as $C_{11}H_{14}O_4^+$ ($[M - HBr - 2\,Br]^+$) and $C_{10}H_{11}O_3^+$ ($[M - OCH_3 - HBr - 2\,Br]^+$) species. Up to this point no skeletal C–C cleavage is noted.[30] In the cases of dibromoene **24a** {*m/z* = 211 (100), 179(22)} and bromodiene **25a** {*m/z* = 211 (51), 179(32)}, analogous cascades produce the corresponding ions. For **17b** ($C_9H_{11}Br_3O_4$), the bromine-free *m/z* = 163 ion $[M - OH - 3\,HBr]^{\cdot+}$ was established as a $C_9H_7O_3^+$ species (HR). In the case of the monocyclic tribromotrione **18** ($C_9H_9Br_3O_3$, Figure 6, top), the first (H)Br is still exclusively lost ($[M]^+$ signal not observed), but the expulsions of the second and third (H)Br (*m/z* = 245, 163) compete with the loss of CO (CH_2CO) {*m/z* = 297 (282)}. The bromine-free *m/z* = 163 ion ($[M - 2\,HBr - Br]^+$, HR) is possibly identical with the $C_9H_7O_3^+$ ion generated from **17b**. In vivid contrast, the anionic spectrum of **18** (Figure 6, bottom) displays only a highly intense $[M]^-$ signal and the neat consecutive loss of $3 \times HBr$ ($C_9H_9O_3Br_3^- \rightarrow C_9H_8O_3Br_2^- \rightarrow C_9H_7O_3Br^- \rightarrow C_9H_6O_3^-$, *m/z* = 162). The very minor signals at the second and third stage are assigned to hydrates of the corresponding unsaturated anions, possibly originating from hydrated **18**.

Clearly, the bromine-free $C_9H_7O_3^+$ and $C_9H_6O_3^-$ ions produced in the vapour phase upon electron-impact ionization are compatible in their compositions with their assignment as protonated and anionic forms of the $C_9H_6O_3$ target molecule **2**. It is understood, though, that these ions might, or even probably, represent a collection of monocyclic or even bi(poly)cyclic isomers with *cis*- and *trans*-C=C double bonds. Figure 7 presents selected calculated structures for the $C_9H_7O_3^+$ (**30**) and $C_9H_6O_3^-$ (**31**) ions with only *cis*-C=C double bonds. As for cation **30**, in its monocylic form structurally very close to the C_2-symmetrical parent minimum conformation **2c**, charge delocalization is largely restricted to a pentadienone segment; a speculatively mediated stabilization as a hydroxy-bishomotropylium ion[31] is not indicated. Of the three anions **31a**–**c**, the C_s-symmetrical **31a** is – unlike in the situation with the neutral **2a** and **2c** – slightly more stable than C_2-symmetrical **31b** (transition

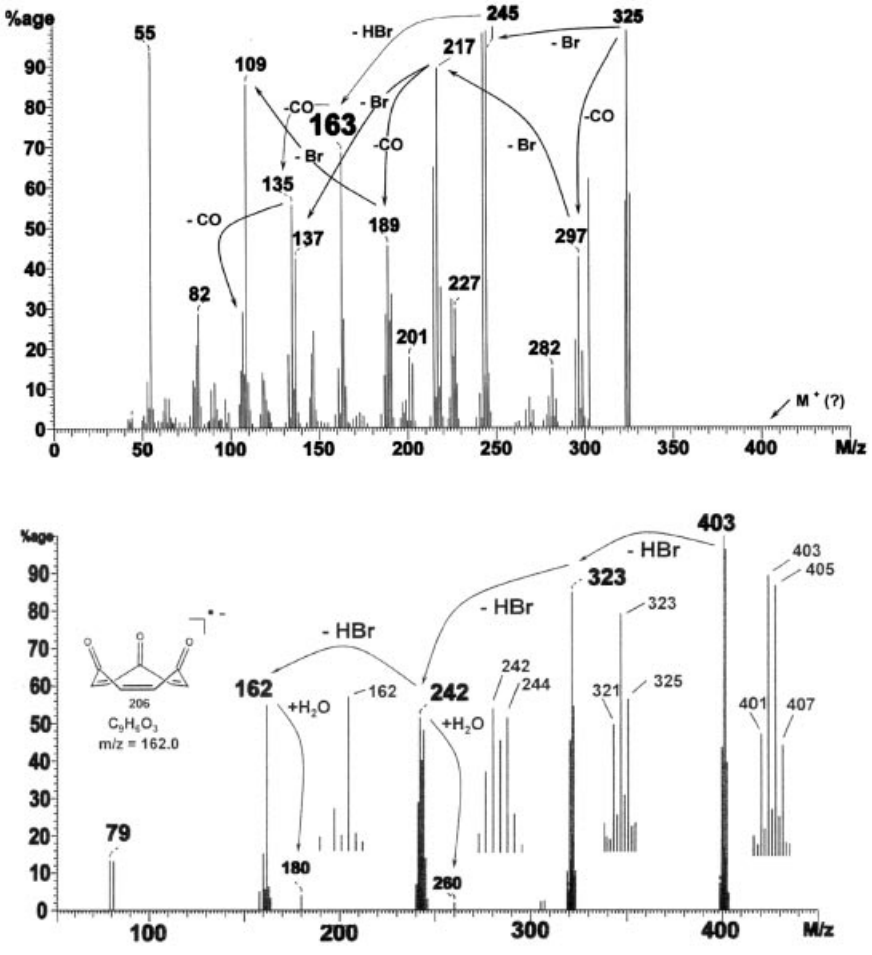


Figure 6. Cationic (top) and anionic (bottom) MS spectra (70 eV) of tribromotrione **18**.

state). Both, however, are significantly less stable than bicyclic *cis*-**31c** (the *trans* isomer of which is higher in energy by 12.4 kcal mol^{-1}, see Supporting Information).

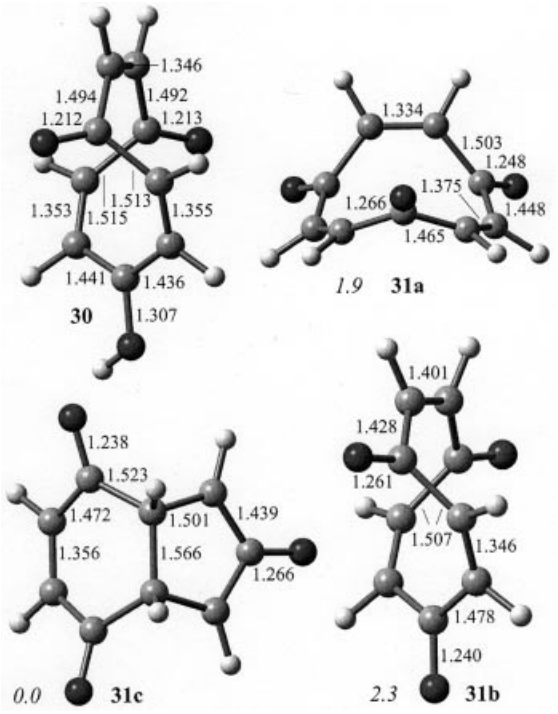


Figure 7. Calculated structures of **30** and **31a**–**c** {B3LYP/6-31+G(d,p),[3] spin unrestricted for **31a**–**c**; distances in Å, *relative energies* in kcal mol^{-1}}.

Concluding Remarks

With the efficiently prepared bicyclic acetals **17** and the monocyclic tribromocyclononanetrione **18**, we once more (cf. **6**) only ostensibly came close to the target trienetrione **2**. The failures with the standard deacetalization and dehydrobromination approaches, partly in line with prior experience,[11,17] underline complications typical in this ballpark of polyfunctionalized, extremely acid- and base-sensitive, medium-sized rings. As for the structures of the $C_9H_9O_3Br_2^-$, $C_9H_8O_3Br^-$, and $C_9H_7O_3^-$ ions so neatly expressed in the anionic MS spectrum of **18**: if sufficiently uniform, their mass-selection in the vapour-phase and subsequent PE analysis, as recently described for the C_{20} fullerene anion,[32] can be visualized as a possible means to clarify this problem, so as possibly to characterize the target molecule **2**.

With this report we close a chapter of chemistry, the varying facets of which have over the years offered lasting stimulation. All had commenced with photochemical investigations directed at the potential of $[2\pi + 2\pi]$ and, as a novelty, $[2\pi + 2\sigma]$ photocycloadditions in organic synthesis, which paved the way to the first, in part singly bridged, *cis*-/*trans*-tris-σ-homobenzenes **A**.[1] As emphasized in the Introduction, the coincident formulation of the Woodward–Hoffman rules[2] had given much impetus to this research program. Subsequently, for both preparative and theoretical purposes, as probes for the concerted natures of the corresponding $3\sigma \rightarrow 3\pi$ isomerization reactions,[33] the X,Y,Z components of **A** were systematically varied (X,Y,Z = O,[34,35] = NR,[36] = S,[37] = $(CH_2)_2$[38]),[39] the three- and four-membered rings were variously mixed[40] and variously bridged,[39,41,42] the six-membered backbones were modified (e.g., hexa-σ-/π-homobenzenes,[43] *cis*/*trans*-tropilidene (tropone)-(tri)oxides[44]). Ultimately, through triple epoxide → cyclopropane conversions, stabilized derivatives (X,Y,Z = $CHCO_2R$, CHCN) of the still unknown, kinetically highly labile parent hydrocarbon **A** (X,Y,Z = CH_2), could be secured.[10] Synthetically, the isomerizations **A** → **C** (X,Y,Z = O, NR) constituted a route to 1,4,7-(hydro)heteronines, an otherwise hardly accessible class of medium-ring heterocycles, as elegant as it was productive.[45] The experimental work launched high-level calculations[46] that confirmed early estimates[33,47] as to the "aromaticity" of the $[\sigma 2s + \sigma 2s + \sigma 2s]$-trishomobenzenoid transition states **B** and related the much higher kinetic stabilities of the triscyclobuta analogues to the "antiaromaticity" of the corresponding transition states. A very rewarding extension of our synthetic activities centered on *cis*-(bis)hetero-bis-σ-homobenzenes (X,Y = NR,NR;[48] O,NR;[49] CHR,NR[50]) and the derived 1,4-(hydro)diheterocines and hydroheterocine anions, another novel class of medium-ring heterocycles.[45] Conflicting theoretical predictions[51] as to the latter's potential "aromaticity" were clarified when N-electron donor/acceptor substitution allowed the isolation of nonplanar, "localized" as well as of planar, "delocalized" rings. Due to their geometries,[52] the *cis*-trioxide and *cis*-triimines **A** became very special tridentate ligands permitting the isolation of metal complexes featuring unusually high coordination (MO_{12}/MN_{12}).[53] Polyfunctionalization combined with efficient synthetic protocols made the trioxides in particular widely applied starting materials for the construction of novel polycyclic systems, some of high theoretical interest [e.g., (aza)octabisvalenes,[54] triaziridines[55]]. As "trisanhydroinositols" these triepoxides ultimately channelled our entry into the area of aminocyclitols[56] and aminoglycoside antibiotics.[57]

In looking back, the senior author (H.P.) expresses his sincere gratitude to his collaborators and to the colleagues who have contributed their advice, expertise and stimulating competition (cf. refs.[35,39,42]). Thanks go to the institutions (DFG, Fonds der Chemie, Humboldt Foundation, BASF AG, Schweizerische Nationalfonds) that have provided generous support.

Experimental Section

General: Melting points were determined on a Monoskop IV instrument (Fa. Bock) and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. Analytical thin layer chromatography (TLC): Merck silica gel plates 60, F_{254} indicator, detection with UV,

$KMnO_4$, *p*-anisaldehyde/H_2SO_4/acetic acid/ethanol. Silica gel used for column chromatography was Merck or ICN Biomedicals GmbH (0.032–0.063 nm). All solvents were carefully dried prior to use. The IR spectra were recorded with a Nicolet Impact 400 FT-IR instrument (KBr pellets), UV/Vis spectra with a Perkin–Elmer Lamda 15 instrument, mass spectra with Finnigan MAT 44S and MAT 312 machines, and NMR spectra with Bruker AC 250, AM 400 and HX 500 instruments. If not specified differently, EI (70 eV) MS, 400/100.6 MHz $^1H/^{13}C$ NMR spectra in $CDCl_3$ are given. Chemical shifts were recorded relative to TMS (δ = 0 ppm); when necessary, assignments were confirmed by homo- and heteronuclear decoupling and H,H and H,X correlation experiments; assignments marked with an asterisk are interchangeable.

1,4,7-Trimethylenecyclononane (9): $Ni(CO)_4$ (52.5 mL, 69.4 g, 0.41 mol) was added under argon to a solution of 3-chloro-2-chloromethylpropene (**8**, 10.7 mL; 12.5 g, 0.10 mol) in carefully dried THF (Na/K, benzophenone, 250 mL), and the solution was immediately transferred into an oil bath preheated to 50 °C. After 68 h the now caramel-coloured solution was concentrated at a maximum of 40 °C/80–100 mbar, the distillate {THF, $Ni(CO)_4$} being condensed at –190 °C. Water (distilled, 200 mL) and *n*-pentane (250 mL) were added to the waxy residue; the mixture was stirred until total dissolution. The greenish aqueous phase was extracted with *n*-pentane (100 mL), and any deposits of $Ni(OH)_2$ were dissolved with HCl (2 N). The combined and dried ($MgSO_4$) organic phase was concentrated over a distillation column with Ag mirror filled with Raschig rings (ca. 60 cm), and the yellowish oily residue (7.6–8.8 g) was fractionated by kugelrohr distillation at 60–95 °C (10^{-2} Torr), giving 2.7–3.1 g (51–57%) of **9** {R_f(cyclohexane) = 0.91} and 475–610 mg (7–9%) of **3,6-dimethylenecyclohexanone** {R_f (ethyl acetate) = 0.8}. ^1H NMR: δ = 4.80 (s, 3×=CH_2), 2.30 (s, 2-,3-,5-,6-,8-,9-H) ppm. ^{13}C NMR: δ = 152.5 (C-1,-4,-7), 112.5 (3 =CH_2), 36.6 (C-2,-3,-5,-6,-8,-9) ppm. IR (KBr): $\tilde{\nu}$ = 3098, 2922 (CH), 2825, 1634 (C=C), 1104, 1022, 898, 845, 786 cm^{-1}. MS: *m*/*z* (%) = 162 (7) $[M]^+$, 147 (90) $[M - CH_3]^+$, 133 (64) $[M - CH_2{-}CH_3]^+$, 105 (88), 91 (100), 79 (83), 77 (38).

Cyclononane-1,4,7-trione (10): a) A solution of **14a** (505 mg, 2.4 mmol) and sulfosalicylic acid (8 mg) in acetone (40 mL) was heated at 40 °C for 2 h and was then concentrated. Acetone (40 mL) was added to the residue, and the solution was again kept at 40 °C for 2 h and then concentrated. This procedure was repeated until total conversion of **14a** (TLC). For workup, $NaHCO_3$ (ca. 30 mg) was added, the reaction solution was concentrated, and the solid residue was chromatographically purified (silica gel, 1×2 cm, cyclohexane/ethyl acetate 1:1, R_f = 0.12). 380 mg (96%) of pure crystals were isolated, m.p. 126 °C. ^1H NMR: δ = 2.62 (s, 6×CH_2) ppm. ^{13}C NMR: δ = 210.5 (C-1,-4,-7), 39.6 (C-2,-3,-5,6,-7,8) ppm. IR: $\tilde{\nu}$ = 2966 (CH), 2925, 1702 (C=O), 1454, 1422, 1387, 1339, 1253, 1234, 1165, 1058 cm^{-1}. MS: *m*/*z* (%) = 168 (11) $[M]^{+\cdot}$, 150 (6), 140 (25) $[M - CO]^{+\cdot}$, 122 (6), 111 (84) $[M - C_3H_4O]^{+\cdot}$, 83 (39), 70 (33), 57 (100), 43 (52). $C_9H_{12}O_3$ (168.2): calcd. C 64.27, H 7.19; found: C 64.40, H 7.58.

Via 14b: A solution of **9** (100 mg, 0.62 mmol) in acetone (20 mL) was slowly added to a deep blue solution of acetone (20 mL) and water (10 mL), saturated at –20 °C with O_3. After total conversion (1 h, TLC), residual O_3 was removed with a stream of N_2, and CH_3SCH_3 (1.5 mL) was added. After 10 min the solution was slowly warmed up to room temperature and, after total reduction (TLC), concentrated at a maximum of 30 °C. The yellowish solid (i.a. **14b**, NMR) was dried for 24 h at 10^{-3} Torr and chromatographed on silica gel (1×2 cm, cyclohexane/ethyl acetate 3:1), and 67 mg of **10** (64%) were isolated (not optimized).

Cyclononane-1,4,7-trione Tris(dimethyl acetal) (11): TMSOTf (0.3 mL, 1.64 mmol) was added by syringe under Ar at –78 °C to a stirred solution of **14a** (88 mg, 0.41 mmol) in anhydrous CH_3OH (6 mL). After 15 min, stirring was continued at –20 °C until total conversion (TLC). Saturated aqueous $NaHCO_3$ solution (1 mL) was added, the solution was concentrated in vacuo, and the residue was dissolved in H_2O (3 mL). After thorough extraction with CH_2Cl_2 the organic phase was dried ($MgSO_4$) and concentrated. The uniform (TLC) oily residue was chromatographed {silica gel, 1×4 cm, cyclohexane/ethyl acetate 2:1; R_f [cyclohexane/ethyl acetate (1:1) = 0.56]}, giving 105 mg (84%) colourless crystals, m.p.: 132 °C. ^1H NMR: δ = 3.15 (s, 6×OCH_3), 1.85 (d, 2-, 3-, 5-, 6-, 8-, 9-H_{endo})*, 1.51 ppm (d, 2-, 3-, 5-, 6-, 8-, 9-H_{exo})*, J = 10.3 Hz. ^{13}C NMR: δ = 105.5 (C-1,-4,-7), 48.4 (6 CH_3), 24.4 (C-2,-3,-5,-6, -8,-9) ppm. IR: $\tilde{\nu}$ = 2982 (CH), 2953, 2896, 2822, 1500, 1463, 1331, 1289, 1232, 1199, 1154, 1104, 1059, 972, 964, 844, 597, 533 cm^{-1}. MS: *m*/*z* (%) = 306 (22) $[M]^+$, 291 (18), 275 (100) $[M - OCH_3]^+$, 260 (44), 202 (8), 151 (5). $C_{15}H_{30}O_6$ (306.4): calcd. C 58.80, H 9.87; found: C 58.54, H 9.92.

Bicyclo[4.3.0]non-1(6)ene-3,9-dione (13): A solution of **10** (78 mg, 0.36 mmol) and HCl (2 N, 1 mL) in CH_3CN/H_2O (1:1) was stirred until total conversion (ca. 4 h). After concentration in vacuo and chromatography {silica gel, 1×3 cm, cyclohexane/ethyl acetate 2:1; R_f (cyclohexane/ethyl acetate 1:1) = 0.09}, 44 mg (81%) of pure crystals were isolated: M.p. 51 °C. ^1H NMR: δ = 2.77 (m, 2a,b-H), 2.64 (m, 8a,b-H)*, 2.47 (m, 4a,b-H)*, 2.42 (m, 5a,b-H)**, 2.32 (m, 7a,b-H)** ppm. ^{13}C NMR: δ = 207.6 (C-9), 207.1 (C-3), 171.3 (C-6), 136.6 (C-1), 37.5 (C-2), 35.6 (C-8)*, 35.4 (C-4)*, 29.6 (C-5)**, 27.8 (C-7)** ppm. IR: $\tilde{\nu}$ = 2941 (CH), 2920, 2830, 1722 (CO), 1693 (CO), 1648 (C=C), 1442, 1429, 1135, 1273, 1236, 1124, 1005, 811, 647 cm^{-1}. MS (CI, NH_3): *m*/*z* (%) = 169 (12) $[M + NH_4]^+$, 151 (100) $[M + H]^+$, 137 (4), 85 (5), 73 (8). $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found: C 72.21, H 6.66.

1,7-Dimethoxy-10-oxabicyclo[5.2.1]decan-4-one (14a): A solution of **9** (1.01 g, 6.20 mmol) in CH_2Cl_2/CH_3OH (1:1, 20 mL) was slowly added to an anhydrous, deep blue solution of CH_2Cl_2 (20 mL) and CH_3OH (20 mL) saturated at –78 °C with O_3. After total conversion (TLC), residual O_3 was removed with a stream of N_2, and CH_3SCH_3 (1.5 mL) was added. After 10 min the solution was slowly warmed up to room temperature and, after total reduction (TLC), concentrated at a maximum of 30 °C. The yellowish solid was dried for 24 h at 10^{-3} bar, adsorbed on to silica gel (1.5 g) and chromatographed on silica gel {2×8 cm, cyclohexane/ethyl acetate 3:1, R_f (cyclohexane/ethyl acetate 1:1) = 0.27}; 1.15 g (86%) of colourless crystals were isolated; m.p. 68 °C. ^1H NMR: δ = 3.30 (s, 2×OCH_3), 2.52 (ddd, 2β-, 3α-, 5α-, 6β-H), 2.31 (ddd, 3β-H, 5β-H), 2.17 (AA′BB′, 8α,β-, 9α,β-H), 1.93 (ddd, 2α-H, 6α-H) ppm; $J_{2\alpha,2\beta}$ = 13.8, $J_{2\alpha,3\alpha}$ = 3.7, $J_{2\alpha,3\beta}$ = 6.8, $J_{2\beta,3\alpha}$ = 10.5, $J_{2\beta,3\beta}$ = 4.0, $J_{3\alpha,3\beta}$ = 13.2 Hz. ^{13}C NMR: δ = 213.7 (C-4), 104.2 (C-1,-7), 49.5 (2 OCH_3), 38.1 (C-3,-5), 36.9 (C-8,-9), 32.2 (C-2,-6) ppm. IR: $\tilde{\nu}$ = 2957 (CH), 2941, 2822, 1689 (CO), 1475, 1343, 1248, 1141, 1087, 980, 902, 873, 857 cm^{-1}. MS: *m*/*z* (%) = 214 (8) $[M]^{+\cdot}$, 196 (5), 182 (38) $[M - CH_3OH]^{+\cdot}$, 165 (15), 157(100), 97 (42), 85(9), 56 (11). $C_{11}H_{18}O_4$ (214.3): calcd. C 61.66, H 8.47; found: C 61.22, H 8.01.

1,7-Dihydroxy-10-oxabicyclo[5.2.1]decan-4-one (14b): DCl/D_2O (33%, 0.1 mL) was added to a solution of **10** (12 mg) in CD_3CN (0.5 mL). Rapidly formed **14b** was analysed in solution: ^1H NMR: δ = 2.83 (m, 3-,5-H), 2.59 (m, 2α-,6α-H), 2.54 (m, 2β-, 6β-H), 2.40 (m, 8α,β-,9α,β-H) ppm. ^{13}C NMR: δ = 180.3 (C-4), 102.3 (C-1,-7), 38.6 (C-3,-5), 36.5 (C-2,-6), 33.2 (C-8,-9) ppm. Various attempts to isolate pure **14b** were fruitless; loss of water led partially back to **10.**

7,7-Dimethoxycyclononane-1,4-dione (15): During attempts to crystallize **11** from acetone without careful exclusion of air (moisture), crystals of **15** suitable for an X-ray structure were serendipitously isolated. ^{1}H NMR: δ = 3.02 (s, 2 × OCH_3), 2.78 (s, 5α,β-,6α,β-H), 2.31 (s, 3α,β-,8α,β-H), 1.42 (2α,β-,9α,β-H) ppm. ^{13}C NMR: δ = 211 (C-1,-4), 105.4 (C-7), 49.7 (2 OCH_3), 39.9 (C-2,-3)*, 37.9 (C-5,-9)*, 27.2 (C-6,-8) ppm.

2β,5β,8β-Tribromo-1,7-dimethoxy-10-oxabicyclo[5.2.1]decan-4-one (17a): a) Carefully dried $PyHBr_3$ (2.25 g, 7.00 mmol) was added to a stirred solution of **14a** (482 mg, 2.25 mmol) in anhydrous CH_3OH (50 mL). After total conversion (TLC), the solution had changed from red to yellow, silica gel (2 g) was added, the reaction solution was concentrated in vacuo, and the solid residue was chromatographed {silica gel, 2.5 × 6 cm, cyclohexane/ethyl acetate 4:1; R_f (cyclohexane/ethyl acetate 1:1) = 0.78}; 920–960 mg (90–95%) of colourless crystals were isolated.

b) A solution of **10** (200 mg, 1.2 mmol) in anhydrous CH_3OH (30 mL) and dry $PyHBr_3$ (1.15 g, 3.6 mmol) was stirred until total conversion (TLC, ca. 4 h). After workup as above, 450 mg (83%) were collected.

c) A solution of **11** (100 mg, 0.33 mmol) in anhydrous CH_3OH (20 mL) and dry $PyHBr_3$ (1.15 g, 3.6 mmol) was stirred until total conversion (TLC, ca. 3 h). After workup as above, 119 mg (80%) were isolated.

Compound 17a: M.p. 149 °C. ^{1}H NMR: δ = 4.72 (dd, 2-H), 4.50 (dd, 5-H), 4.36 (dd, 8-H), 3.32 (s, OCH_3), 3.30 (s, OCH_3), 3.26 (dd, 3β-H), 2.80 (dd, 3α-H), 2.15 (m, 6α,β-, 9α,β-H) ppm; $J_{2,3\alpha}$ = 4.5, $J_{2,3\beta}$ = 12, $J_{3\alpha,3\beta}$ = 12.6, $J_{5,6\alpha}$ = 8, $J_{5,6\beta}$ = 11.5, $J_{6\alpha,6\beta}$ = 14, $J_{8,9\alpha}$ = 5, $J_{8,9\beta}$ = 12.3, $J_{9\alpha,9\beta}$ = 15 Hz. ^{13}C NMR: δ = 197.8 (C-4), 110.2 (C-7), 106.5 (C-1), 49.9 (OCH_3), 49.1 (OCH_3), 48.9 (C-8), 47.7 (C-2), 44.1 (C-9), 41.3 (C-5),41.2 (C-6), 39.8 (C-3) ppm. IR: $\tilde{\nu}$ = 2987 (CH), 2945, 2834, 1718 (C=O), 1462, 1359, 1322, 1240, 1145, 1104, 1050, 989, 861, 754, 671, 577 cm^{-1}. MS: *m/z* (%) = [455 (3), 453 (8), 451 (8), 449 (4)] $[M + H]^+$, [422 (3), 421 (3), (7), 419 (8), 417 (4)] $[M - OCH_3]^+$, [373 (14), 371 (20), 369 (10)] $[M - Br]^+$, [341 (44), 339 (76), 337 (38)] $[M - OCH_3 - Br]^+$, [291 (48), 289 (41)] $[M - 2(H)Br]^+$, [261 (54), 259 (100), 257 (42)] $[M - OCH_3 - 2Br]^+$, 235 (19), 211 (21) $[M - 3Br]^+$, 179 (40) $C_{10}H_{11}O_3$ (HR), $[M - OCH_3 - HBr - 2Br]^+$, 97(28), 55 (43). $C_{11}H_{15}Br_3O_4$ (451.0): calcd. C 29.30, H 3.35, Br 53.16; found: C 29.02, H 3.48, Br 52.21.

2β,5β,8β-Tribromo-1,7-dihydroxy-10-oxabicyclo[5.2.1]decan-4-one (17b): A suspension of **10** (300 mg, 1.80 mmol) and $PyHBr_3$ (1.86 g, 5.80 mmol) in anhydrous *tert*-butyl alcohol (35 mL) was stirred until total conversion (ca. 6 h). After concentration, the residue (containing **18** as nearly exclusive product, TLC) was adsorbed on silica gel (600 mg) and chromatographed (silica gel, 3 × 7 cm, cyclohexane/ethyl acetate 3:1); 644 mg (85%) of colourless solid **17b** {R_f (cyclohexane/ethyl acetate 1:1) = 0.32} were isolated; m.p. 64 °C. ^{1}H NMR (CD_3CN): δ = 4.96 (s, OH), 4.73 (s, OH), 4.35 (dd, 5-H), 4.32 (dd, 2-H), 4.27 (dd, 8-H), 3.40 (dd, 6β-H), 2.75 (2 × dd, 3β-, 9β-H), 2.63 (dd, 6α-H), 2.49 (2 × dd, 3α-, 9α-H) ppm; $J_{2,3\alpha}$ = 4.3, $J_{2,3\beta}$ = 8.4, $J_{3\alpha,3\beta}$ = 14.2, $J_{5,6\alpha}$ = 4.6, $J_{5,6\beta}$ = 8.4, $J_{6\alpha,6\beta}$ = 12.8, $J_{8,9\alpha}$ = 7.3, $J_{8,9\beta}$ = 12.2, $J_{9\alpha,9\beta}$ = 12.5 Hz. ^{13}C NMR (CD_3CN): δ = 199.6 (C-4), 107.7 (C-7), 104.8 (C-1), 56.1 (C-5), 50.5 (C-2), 49.5 (C-8), 43.8 (C-6), 41.8 (C-3), 40.5 (C-9) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (OH), 2965, 2935 (CH), 2845, 1703 (C=O), 1453, 1308, 1176, 968, 902, 754 cm^{-1}. MS (CI, isobutane): *m/z* (%) = {427 (32), 425 (95), 423 (100), 421 (35)} $[M + H]^+$, {407, 405, 403, 401} $[M - H_2O]^+$, [389 (15), 387 (16)] $[M + H - 2H_2O]^+$, [327 (30), 325 (100), 323 (32)] $[M - H_2O - Br]^+$, 307 (16) $[M - 2H_2O - Br]^+$, 299 (2), 297 (6), 295 (2), 267 (11), {245 (52), 243 (37)} $[M - H_2O - Br - HBr]^+$, [227 (15), 225 (9)] $[M - 2H_2O - Br - HBr]^+$, 165 (18), 163 (16) ($C_9H_7O_3$, HR), $[M - H_2O - 2HBr - Br]^+$ 137 (9), 135 (8) ($C_8H_7O_2$, HR) $[M - H_2O - 2HBr - Br - CO]^+$, 109 (10). $C_9H_{11}Br_3O_4$ (422.9): calcd. C 25.56, H 2.62, Br 56.68; found: C 25.87, H 2.813, Br 55.33. X-ray structure.[21]

2β,5β,8β-Tribromo-1,7-bis(trimethylsilyloxy)-10-oxabicyclo[5.2.1]decan-4-one (17c): An anhydrous solution of **17b** (102 mg, 0.24 mmol) and TMSCN (0.2 mL, 1.60 mmol) in CH_2Cl_2 (20 mL) was heated at reflux for 14 h. After concentration, the oily residue was filtered through silica gel (1 × 1.5 cm, cyclohexane/ethyl acetate 3:1) to afford 122 mg (89%) of a uniform fraction (TLC) as a colourless oil {R_f (cyclohexane/ethyl acetate 4:1) = 0.69}. ^{1}H NMR (CD_3CN): δ = 4.39 (dd, 5-H), 4.32 (dd, 2-H), 4.23 (dd, 8-H), 3.40 (dd, 6β-H), 2.86 (dd, 3β-H), 2.74 (dd, 9β-H), 2.66 (dd, 6α-H), 2.49 (2 × dd, 2α-, 9α-H), 0.12 [s, $Si(CH_3)_3$], 0.09 [s, $Si(CH_3)_3$] ppm; $J_{2,3\alpha}$ = 4.3, $J_{2,3\beta}$ = 13.1, $J_{3\alpha,3\beta}$ = 15.2, $J_{5,6\alpha}$ = 4.6, $J_{5,6\beta}$ = 12.8, $J_{6\alpha,6\beta}$ = 13.1, $J_{8,9\alpha}$ = 7.3, $J_{8,9\beta}$ = 12.2, $J_{9\alpha,9\beta}$ = 14.0 Hz. ^{13}C NMR (CD_3CN): δ = 199.3 (C-4), 109.1 (C-7), 106.9 (C-1), 57.2 (C-5), 52.6 (C-2), 49.5 (C-8), 45.4 (C-6), 44.0 (C-3), 41.5 (C-9), 1.5 [$Si(CH_3)_3$], 0.97 [$Si(CH_3)_3$] ppm. IR: $\tilde{\nu}$ = 2933 (CH), 1726 (C=O), 1470, 1310, 1269, 1120, 1026, 989, 944, 844, 762, 564 cm^{-1}. MS: *m/z* (%) = {571 (53), 569 (90), 567 (100) 565 (52)} $[M + H]^+$, 491 (41), 489 (81), 487 (70), 407 (19), 405 (9), 403 (4). $C_{15}H_{27}Br_3O_4Si_2$ (567.3).

2α,5α,8α-Tribromocyclononane-1,4,7-trione (18): An anhydrous solution of **17a** (180 mg, 0.40 mmol) and BBr_3 (300 mg, 1.20 mmol) in benzene (10 mL) was kept at 3 °C until total conversion (ca. 5 h). After concentration in vacuo at 0 °C, dry cyclohexane (12 mL) was added, the mixture was sonicated for 5 min, and the yellowish solid was filtered off and dried at 10^{-4} Torr to afford 152 mg (93%) of a yellowish crystalline solid {R_f (cyclohexane/ethyl acetate 1:1) = 0.47}; m.p. 178 °C (dec). ^{1}H NMR (C_6D_6): δ = 4.05 (dd, 2-, 5-, 8-H), 2.69 (dd, 3-,6-,9-H_{endo}), 2.10 (dd, 3-,5-,9-H_{exo}) ppm; $J_{2,3endo}$ = 12.5, $J_{2,3exo}$ = 5.8, $J_{3endo,3exo}$ = 14.9 Hz. ^{13}C NMR (C_6D_6): δ = 196.3 (C-1,-4,-7), 48.9 (C-2,-5,-8), 39.2 (C-3,-6,-9) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (CH), 2864, 1705 (C=O), 1467, 1302, 1108, 993, 857, 688, 548, 437 cm^{-1}. MS Figure 6 (neg. CI, isobutane, 170 eV): *m/z* (%) = {407 (30), 405 (92), 403 (100), 401(38)} $[M - H]^-$, {325 (60), 323 (80) 321 (55)} $[M - H - HBr]^-$, 260 (5), 246 (16), 244 (48), 243 (41), 242(51) 241 (29), 180(6), 162 (54) ($C_9H_6O_3$, HR), $[M - 3HBr]^{\cdot-}$, 81, 79. MS (EI, 70 eV): *m/z* = [327 (62), 325 (100), 323 (60)] $[M - Br]^+$, 303 (65), [299 (20), 297 (48), 295 (22)] $[M - Br - CO]^{\cdot+}$, [284 (8), 282(17), 280 (8)] $[M - Br - CH_3CO]^+$, [245 (95), 243 (93)] $[M - Br - HBr]^+$, 227 (31), 219 (38), [217 (86), 215 (68)] $[M - Br - HBr - CO]^+$, 191 (32), 189 (44), 187 (28) $[M - 2(H)Br - 2CO]^+$, 163 (68) $[M - 2HBr - Br]^+$ {HR: calcd. 163.039520 ($C_9H_7O_3$); found: 163.039523}, 137 (40), 135 (55), 109 (84), 82 (29), 55 (93). $C_9H_9Br_3O_3$ (404.9): calcd. C 26.70, H 2.24, Br 59.21; found: C 26.04, H 2.40, Br 58.33. In contact with moisture **17b** is formed.

5β,8β-Dibromo-1,7-dimethoxy-10-oxabicyclo[5.2.1]dec-2-en-4-one (24a): An anhydrous solution of **17a** (200 mg, 0.44 mmol) and DBU (0.66 mL, 4.4 mmol) in toluene (50 mL) was stirred under Ar at 50 °C until total conversion (TLC, ca. 2 h). The brownish solution with the precipitate (DBU·HBr) was concentrated in vacuo, and the solid residue was chromatographed (silica gel, 1.5 × 4 cm, cyclohexane/ethyl acetate 3:1). After the major component {R_f (**24a**) (cyclohexane/ethyl acetate 1:1) = 0.62, 134 mg, 82%}, a very minor one {R_f (**25a**; cyclohexane/ethyl acetate 1:1) = 0.58, 4 mg, 3%} was also eluted. **Compound 24a**: Colourless crystals, m.p. 134 °C. ^{1}H NMR: δ = 6.22 (d, 2-H), 5.89 (d, 3-H), 4.52 (dd, 5-H), 4.46 (dd, 8-H), 3.37 (s, OCH_3), 3.22 (s, OCH_3), 2.79 (dd, 9α-H), 2.68 (dd, 6α-H), 2.51 (dd, 6β-H), 2.45 (dd, 9β-H) ppm; $J_{2,3}$ = 11.2, $J_{5,6\alpha}$ = 4.3, $J_{5,6\beta}$ = 12.5, $J_{6\alpha,6\beta}$ = 14.4, $J_{8,9\alpha}$ = 9.3, $J_{8,9\beta}$ = 10.7, $J_{9\alpha,9\beta}$ = 14.2 Hz. ^{13}C NMR: δ = 198.3 (C-4), 136.8 (C-3), 126.4 (C-2),

108.7 (C-7), 103.8 (C-1), 51.3 (OCH_3), 49.7 (OCH_3), 47.6 (C-8), 45.2 (C-9), 42.6 (C-6), 40.2 (C-5) ppm. IR: $\tilde{\nu}$ = 3007 (CH), 2953, 2854, 1706 (C=O), 1466, 1368, 1297, 1195, 1133, 1096, 1001, 877, 742, 461 cm^{-1}. UV (CH_3CN): λ_{max} (ε) = 290 nm (70), 199 (10280) cm^{-1}. MS (CI, isobutane): *m/z* (%) = [373 (31), 371 (90), 369 (33)] $[M + H]^+$, [339 (5), 337 (5)] $[M - OCH_3]^+$, [293 (40), 291(45)] $[M - Br]^+$, [261 (5), 259 (6)] $[M - OCH_3 - HBr]^+$, 211 (100) $[M - Br - HBr]^+$, 179 (22) ($C_{10}H_{11}O_3$, HR), $[M - OCH_3 - 2Br]^+$. $C_{11}H_{14}Br_2O_4$ (370.0): calcd. C 35.70, H 3.81, Br 43.19; found: C 36.11, H 3.99, Br 42.11.

8β-Bromo-1,7-dimethoxy-10-oxabicyclo[5.2.1]deca-2,5-dien-4-one (25a): Cf. **24a**. This compound was obtained from **17a** (228 mg, 0.51 mmol), by treatment with DBU (1.90 mL, 12.6 mmol) in toluene (50 mL) at 80 °C (5 h). After chromatographic workup, 47 mg (25%) of **24a** and 90 mg (61%) of **25a** were isolated. **Compound 25a**: Colourless crystals, m.p. 101 °C. ^{1}H NMR: δ = 6.22 (dd, 2-H), 6.10 (d, 6-H), 6.05 (d, 3-H), 5.90 (dd, 5-H), 4.50 (dd, 8-H), 3.37 (s, OCH_3), 3.32 (s, OCH_3) 2.69 (dd, 9α-H), 2.49 (dd, 9β-H) ppm; $J_{2,3}$ = 11.4, $J_{5,6}$ = 11.2, $J_{8,9\alpha}$ = 7.5, $J_{8,9\beta}$ = 12.5, $J_{9\alpha,9\beta}$ = 13.3 Hz. ^{13}C NMR: δ = 199.8 (C-4), 137.8 (C-2), 135.3 (C-6), 131.8 (C-3), 130.0 (C-5), 107.5 (C-7), 105.1 (C-1), 52.3 (OCH_3), 51.0 (OCH_3), 50.0 (C-8), 45.7 (C-9) ppm. IR: $\tilde{\nu}$ = 2941 (CH), 2834, 1701 (CO), 1639 (C=C), 1442, 1376, 1282, 1166, 1017, 981, 873, 787, 721, 676, 644 cm^{-1}. MS (CI, isobutane): *m/z* (%) = {291 (82), 289 (100)} $[M + H]^+$, {259 (12), 257 (13)} $[M - OCH_3]^+$, 211 (51), 209 (30) $[M - Br]^+$, 179 (32) ($C_{10}H_{11}O_3$, HR)$[M - 2OCH_3 - Br]^+$, 151 (12), 125 (16), 87 (88). $C_{11}H_{13}BrO_4$ (289.1): calcd. C 45.70, H 4.53, Br 27.64; found: C 45.12, H 4.66, Br 26.98.

1,7-Dimethoxy-10-oxabicyclo[5.2.1]deca-2,5,8-trien-4-one (26a): Cf. **24a**. This compound was obtained from **17a** (300 mg, 0.67 mmol), by treatment with DBU (4.00 mL, 26.6 mmol) in toluene (75 mL) at reflux (12 h, one product, TLC). After chromatographic workup (silica gel, 1.5 × 5 cm), 120 mg (85%) of colourless crystals were isolated; m.p. 84 °C {R_f (cyclohexane/ethyl acetate 1:1) = 0.25}. ^{1}H NMR (C_6D_6): δ = 5.63 (d, 2-, 6-H), 5.49 (d, 3-, 5-H), 5.38 (s, 8-H,9-H), 3.12 (s, $2OCH_3$) ppm; $J_{2,3}$ = $J_{5,6}$ = 11.3 Hz. ^{13}C NMR (C_6D_6): δ = 200.4 (C-4), 133.4 (C-3,-5), 131.0 (C-2,-6), 129.9 (C-8, -9), 110.0 (C-1,-7), 50.9 (2 OCH_3) ppm. IR: $\tilde{\nu}$ = 3003, 2976 (CH), 1702 (C=O), 1634 (C=C), 1457, 1422, 1387, 1338, 1219, 1202, 1138, 1098, 987, 503 cm^{-1}. UV (CH_3CN): λ_{max} (ε) = 314 (20), 229 (985, sh), 200 nm (11200). MS: *m/z* (%) = 208 (12) $[M]^+$, 193 (7), 179 (22), 163 (3), 149 (54), 121 (33) 113 (7), 95 (9). $C_{11}H_{12}O_4$ (208.2): calcd. C 63.45, H 5.81; found: C 62.88, H 5.98.

6β-Bromo-1,7-dimethoxy-10-oxabicyclo[5.2.1]deca-2,8-dien-4-one (27): An anhydrous solution of **26a** (40 mg, 0.19 mmol) and bromocatecholborane (76 mg, 0.38 mmol) in CH_2Cl_2 (20 mL, argon) was stirred until total conversion (TLC, ca. 4 h). After evaporation in vacuo and drying at 10^{-4} Torr the nearly uniform solid residue (TLC) was spectroscopically characterized as such {R_f (cyclohexane/ethyl acetate 1:1) = 0.61}. ^{1}H NMR: δ = 6.18 (d, 2-H), 6.08 (d, 3-H), 6.04 (d, 8-H) 5.90 (d, 9-H), 4.34 (dd, 6-H), 3.33 (s, OCH_3), 3.24 (s, OCH_3) 3.20 (dd, 5α-H), 2.59 (dd, 5β-H) ppm; $J_{2,3}$ = 11.4, $J_{5\alpha,5\beta}$ = 13.4, $J_{5\alpha,6\alpha}$ = 3.3, $J_{5\beta,6\alpha}$ = 13.2, $J_{8,9}$ = 5.8 Hz. ^{13}C NMR: δ = 198.4 (C-4), 137.9 (C-2), 136.8 (C-3), 134.5 (C-8), 134.1 (C-9), 106.8 (C-7), 106.1 (C-1), 54.5 (C-6), 50.7 (OCH_3), 50.0 (OCH_3), 46.3 (C-5) ppm. MS (CI, isobutane): *m/z* (%) = {291 (66), 289 (100)} $[M + H]^+$, {259 (15), 257 (17)} $[M - OCH_3]^+$, 209 (12), $[M - Br]^+$, 195 (47), 179 (21) $[M - Br - 2OCH_3]^+$ ($C_{10}H_{11}O_3$, HR), 167 (41), 151 (13), 125 (9). $C_{11}H_{13}BrO_4$ (289.1).

(2β,7β)-1,11-Dimethoxy-14,15-dioxatetracyclo[9.2.1.1^{3,6}.0^{2,7}]pentadeca-4,9,12-trien-8-one (28a): A degassed, anhydrous mixture of **26a** (45 mg, 0.22 mmol), furan (0.2 mL) and diethyl ether (0.2 mL), in a welded Teflon tube, was heated at 60 °C/12 kbar for 12 d. After concentration, the solid residue (54 mg, one product besides residual **26a**, ca. 1:3, TLC, ^{1}H NMR) was chromatographed (silica gel, 1 × 4 cm, cyclohexane/ethyl acetate 4:1); 15–20% of the produced **28a** underwent retro-Diels–Alder cleavage. **Compound 28a** {R_f (cyclohexane/ethyl acetate 1:1) = 0.18}: 7 mg (11%), colourless crystals. ^{1}H NMR (500 MHz):δ = 6.84 (dd, 10-H), 6.50 (dd, 9-H), 6.06 (d, 12-H), 5.91 (d, 5-H), 5.78 (d, 13-H), 5.72 (d, 4-H), 4.9–5.0 (m, 3-,6-H), 3.47 (m, 7-H), 3.35 (m, 2-H), 3.30 (s, OCH_3), 3.13 (s, OCH_3) ppm; $J_{2,3}$ = 4.5, $J_{2,7}$ = 10.5, $J_{4,5}$ = 6.0, $J_{9,10}$ = 11.2, $J_{12,13}$ = 6.0 Hz. ^{13}C NMR: δ = 204.2 (C-8), 136.7 (C-10), 135.1 (C-9), 133.0 (C-5), 132.9 (C-4), 132.3 (C-13), 132.1 (C-12), 111.4 (C-1), 111.1 (C-11), 80.9 (C-3), 80.8 (C-6), 58.9 (OCH_3), 56.9 (OCH_3), 52.2 (C-7), 50.2 (C-2) ppm. MS: *m/z* (%) = 277 (8) $[M + H]^+$, 244 (28) $[M - CH_3OH]^+$, 220 (8), 216 (7), 192 (20), 182 (22), 122 (41), 69 (100) $[C_4H_4O + H]^+$, $C_{15}H_{16}O_5$ (276.3).

(2β,7β)-1,4,5,11-Tetramethoxy-14,15-dioxatetracyclo[9.2.1.1^{3,6}0^{2,7}]-pentadeca-4,9,12-trien-8-one (28b) and (2β,7β,9β,14β)-1,4,5,11,12,15-Hexamethoxy-18,19,20-trioxahexacyclo[13.2.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]dodeca-4,11,16-trien-8-one (29b): Cf. **28a**. These compounds were obtained from **26a** (64 mg, 0.30 mmol) and 3,4-dimethoxyfuran (0.4 mL) in ether (0.4 mL) at room temp., 15 kbar. Besides residual **26a**, two products (8:3:1; TLC, ^{1}H NMR). Chromatographically (silica gel, 1 × 4 cm, cyclohexane/ethyl acetate 4:1), 24 mg (26%) of a 4:1 mixture of **28b** and **29b** were separated {R_f (cyclohexane/ethyl acetate 1:1) = 0.30/0.29; ca. 15% of **28b** and ca. 25% of **29b** were lost through retro-DA}. **Compound 28b**: ^{1}H NMR (500 MHz): δ = 6.06 (dd, 12-H), 6.02 (dd, 10-H), 5.85 (d, 9-H), 5.84 (d, 13-H), 5.28 (d, 6-H), 5.05 (d, 3-H), 3.74 (s, OCH_3), 3.71 (s, OCH_3) 3.48 (s, OCH_3), 3.22 (s, OCH_3), 3.10 (d, 7-H), 3.00 (d, 2-H) ppm; $J_{2,3}$ = 1.7, $J_{2,7}$ = 9.3, $J_{9,10}$ = 11.0, $J_{12,13}$ = 5.7 Hz. ^{13}C NMR: δ = 204.2 (C-8), 140.7 (C-4), 140.1 (C-5), 133.4 (C-10), 133.4 (C-13), 133.2 (C-9), 131.8 (C-12), 111.6 (C-11), 110.5 (C-1), 78.7 (C-6), 78.6 (C-3), 59.0 (OCH_3), 59.0 (OCH_3), 58.9 (OCH_3), 57.0 (OCH_3), 52.0 (C-7), 50.8 (C-2) ppm. MS (CI, isobutane): *m/z* (%) = 465 (4) [**29b** + H].$^+$, 450 (15) [**29b** + H – CH_3]$^{\cdot+}$, 434 (17) [29b + H – OCH_3].$^+$, 402 [**29b** – $2OCH_3$]$^{\cdot+}$, 377 (7), 355 (22), 337 (55) [**28b** + H]$^{\cdot+}$, 322 (**28b** + H – CH_3)$^{\cdot+}$, 306 [**28b** + H – OCH_3]$^+$, 278 (45), 223 (15), 128 (100) $[C_6H_8O_3]^{\cdot+}$, 76 (12). $C_{17}H_{20}O_7$ (336.3). **Compound 29b**: ^{1}H NMR (500 MHz): δ = 5.88 (s, 16-,17-H), 4.86 (m, 6-,10-H), 4.75 (m, 3-, 13-H), 3.84 (s, 2 × OCH_3), 3.76 (s, 2 × OCH_3), 3.49 (m, 7-,9-H), 3.18 (s, 2 × OCH_3), 3.24 (m, 2-,14-H) ppm. ^{13}C NMR: δ = 204.6 (C-8), 139.3 (C-5,-11), 139.0 (C-4,-12), 133.2 (C-16,-17), 110.4 (C-1,-15), 80.0 (C-6,-10), 79.7 (C-3,-13), 59.2 (2 OCH_3), 59.0 (2 OCH_3), 58.9 (2 OCH_3), 51.8 (C-7,-9), 50.1 (C-2, -14) ppm. **28b**: $C_{17}H_{20}O_7$ (336.3). **29b**: $C_{23}H_{28}O_{10}$ (464.2).

Supporting Information (see also the footnote on the first page of this article): Cartesian coordinates for the calculated structures (Å) **1**, **2a**, **2b**, **2c**, **3**, **6**, **7**, **10**, **14a**, **18**, *cis*-**24a**, *trans*-**24a**, *cis*,*cis*-**25a**, *cis*,*trans*-**25a**, **30**H$^+$, **31a**, **31b**, **31c** and **31d**. X-ray structure of **17b**.

Acknowledgments

Thanks go to Prof. Dr. R. Schwesinger for force-field calculations, to G. Fehrenbach for artwork, to M. Bär for technical assistance, to Dr. P. R. Spurr for help with the manuscript, to the BASF AG for a generous gift of $Ni(CO)_4$, and to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

[1] a) H. Prinzbach, W. Eberbach, G. Philippossian, *Angew. Chem.* **1968**, *80*, 910; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 887; b) H.

Prinzbach, M. Klaus, W. Mayer, *Angew. Chem.* **1969**, *81*, 902; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 883; c) H. Prinzbach, D. Stusche, *Angew. Chem.* **1970**, *82*, 836; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 799; d) H. Prinzbach, D. Stusche, *Helv. Chim. Acta* **1971**, *54*, 755; e) D. Stusche, M. Breuninger, H. Prinzbach, *Helv. Chim. Acta* **1972**, *55*, 2359.

[2] a) R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781; b) M. J. Goldstein, R. Hoffmann, *J. Am. Chem. Soc.* **1971**, *93*, 6193; c) J. A. Berson, S. S. Olin, E. W. Petrillo Jr, P. Bickart, *Tetrahedron* **1974**, *30*, 1639; d) J. Spanget-Larsen, R. Gleiter, *Angew. Chem.* **1978**, *90*, 471; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 441. Cf. The more recent evaluation of neutral trishomoaromaticity in a tris(bismethano)benzene: F. Stahl, P. v. R. Schleyer, H. Jiao, H. F. Schaefer III, K.-H. Chen, N. L. Allinger, *J. Org. Chem.* **2002**, *67*, 6599, and cited references.

[3] All structures were optimized with the Gaussian 03 program package[4] at the B3LYP/6-31+G(d,p) level,[5–8] starting with RHF/6-31+G(d,p)-orbitals as initial guess (SCF convergence criteria for density matrix [r. m. s.] and energy: 10^{-8} and 10^{-6}; optimization convergence criteria for maximum force and maximum displacement: 4.5×10^{-4} and 1.8×10^{-3}). The default (75302) grid (*FineGrid*) was employed for numerical integration. Cartesian d-functions were used throughout. Unless otherwise stated, all structures are minima according to their Hessian eigenvalues. The validity of the single reference calculations was checked in all cases by a stability analysis.[9].

[4] *Gaussian 03*, Revision B.04: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian, Inc*., Pittsburgh PA, **2003**.

[5] A. D. Becke, *J. Chem. Phys.* **1997**, *107*, 8554.

[6] A. D. Becke, *J. Chem. Phys.* **1996**, *104*, 1040.

[7] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[8] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[9] R. Bauernschmitt, R. Ahlrichs, *J. Chem. Phys.* **1996**, *104*, 9047.

[10] a) E. g. W.-D. Braschwitz, T. Otten, C. Rücker, H. Fritz, H. Prinzbach, *Angew. Chem.* **1989**, *101*, 1383; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1348; b) C. Rücker, H. Müller-Bötticher, W.-D. Braschwitz, H. Prinzbach, U. Reifenstahl, H. Irngartinger, *Liebigs Ann./Recueil* **1997**, 967. For early attempts ending in carbocyclic *trans*-tris-σ-homobenzenes see: H. Prinzbach, R. Schwesinger, *Angew. Chem.* **1972**, *84*, 988; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 940.

[11] G. Person, M. Keller, H. Prinzbach, *Liebigs Ann.* **1996**, 507, and cited references.

[12] For early unsuccessful attempts to prepare **10** see: a) S. Kawai, S. Tanaka, U. Terai, M. Tezuka, T. Nishivhi, *Bull. Chem. Soc. Jpn.* **1960**, *33*, 669; b) S. Kawai, S. Tanaka, *Bull. Chem. Soc. Jpn.* **1960**, *33*, 674.

[13] Compound **9** is readily accessible by treatment of 3-chloro-2-chloromethylpropene (**8**) with $Ni(CO)_4$: a) E. J. Corey, M. F. Semmelhack, *Tetrahedron Lett.* **1966**, *7*, 6237; b) M. F. Semmelhack, *Org. Reactions* vol. 5, chapter 2, p. 105; c) E. J. Corey, P. Helquist, *Tetrahedron Lett.* **1975**, *16*, 4091. Under standardized conditions, we have routinely collected 3 g batches of **9** (up to 60% together with up to 5% of 1,4-dimethylenecyclohexane and 10% of 3,6-dimethylenecycloheptanone).[15].

[14] Efforts to prepare **2** in analogy to **9** by "cyclotrimerization" of propynal (C_3H_2O) mediated by $Ni(CO)_4$ gave, as reported (F. Wille, W. Schwab, *Monatsh. Chem.* **1977**, *108*, 929), small quantities of benzene-1,3,5-tricarbaldehyde.[15] From the reaction of cyclopropenone (C_3H_2O) with $Ni(COD)_2$ as dimer, *p*-benzoquinone and as trimer, a lactone have been obtained (R. Noyori, I. Umeda, *Chem. Lett.* **1972**, 1189).

[15] A. Pleschke, Dissertation, University of Freiburg, **2000**.

[16] M. Oda, Y. Kayama, H. Miyazaki, Y. Kitahara, *Angew. Chem.* **1975**, *87*, 414; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 418.

[17] P. A. Chaloner, A. B. Holmes, M. A. McKervey, R. A. Raphael, *J. Chem. Soc. Perkin Trans. 1* **1977**, 2524.

[18] a) J. E. Baldwin, D. P. Kelly, *J. Chem. Soc. Chem. Commun.* **1968**, 1664; b) T. Sato, K. Uno, *J. Chem. Soc. Perkin Trans. 1* **1973**, 895; c) T. Yamamoto, N. Sakaue, *J. Chem. Res. Miniprint* **1997**, 2610. For a discussion of various bromination/dehydrobromination procedures applied to (bridged)medium-sized ketones and complications met, see: H. Quast, C. Beckler, E. Geißler, K. Knoll, E.-M. Peters, K. Peters, H.-G. v. Schnering, *Liebigs Ann. Chem.* **1994**, 109, and cited references.

[19] P. Binger, H. Schaefer, R. Goddard, *J. Chem. Soc. Perkin Trans. 2* **1993**, 633; cf. cyclononane: a) M. Deleuze, J. Delhalle, T. Pickup, *J. Phys. Chem.* **1994**, *98*, 2382; b) O. V. Dorofeeva, V. S. Mastryukov, N. L. Allinger, A. Almenningen, *J. Phys. Chem.* **1990**, *94*, 8044.

[20] a) M. Karplus, *J. Am. Chem. Soc.* **1963**, *85*, 2870; b) H. Günther, *NMR-Spektroskopie*, 3. Auflage, p. 188 ff, Thieme, Stuttgart, **1992**.

[21] CCDC-645743 (for **11**), -645741 (for **15**), -645740 (for **17a**), -645745 (for **17b**), -645742 (for **24a**) and -645744 (for **26a**) 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).

[22] A. Marquet, H. B. Kagan, L. Mamlok, J. Jaques, *Bull. Soc. Chim. Fr.* **1961**, 1822.

[23] G. Simchen, W. Kober, *Synthesis* **1976**, 259.

[24] G. A. Olah, B. G. B. Gupta, S. C. Narang, R. Malhotra, *J. Org. Chem.* **1979**, *44*, 4272.

[25] E. J. Corey, Y. J. Wu, *J. Am. Chem. Soc.* **1993**, *115*, 8871.

[26] *t*BuP1 = *tert*-Butyliminotris(dimethylamino)phosphorane: R. Schwesinger, H. Schlemper, C. Hasenfratz, J. Willaredt, T. Dambacher, T. Breuer, C. Ottaway, M. Fletschinger, J. Boele, H. Fritz, D. Putzas, H. W. Rotter, F. G. Bordwell, A. V. Satish, G.-Z. Ji, E.-M. Peters, K. Peters, H. G. v. Schnering, L. Walz, *Liebigs Ann.* **1996**, 1055, and cited references.

[27] P_2F = Hexakis(dimethylamino)diphosphazenium fluoride: R. Schwesinger, R. Link, P. Wenzl, S. Kossek, *Chem. Eur. J.* **2006**, *12*, 438.

[28] a) R. K. Boeckman Jr, J. C. Potenza, *Tetrahedron Lett.* **1985**, *26*, 1411; b) P. F. King, S. G. Stroud, *Tetrahedron Lett.* **1985**, *26*, 1415.

[29] Monoaddition of furan to *p*-quinone was achieved at 20 kbar/room temp., bisaddition at 22 kbar/60 °C; 3,4-dimethoxyfuran added at room temperature without pressure: a) J. Jurczak, T. Kozluk, S. Filipek, C. H. Eugster, *Helv. Chim. Acta* **1983**, *66*, 222; b) A. A. Hofmann, J. Wyrsch-Walraf, P. X. Iten, C. H. Eugster, *Helv. Chim. Acta* **1979**, *62*, 2211.

[30] G. Haufe, W. Hein, G. Graefe, *J. Prakt. Chem.* **1978**, *320*, 91.

[31] See p. 222 ff in: *Structure and Dynamics of $C_9H_9^+$ Ions: An Experimental and Theoretical Comparison* in *Stable Carbocation Chemistry* (Eds.: G. K. S. Prakash, P. v. R. Schleyer), Wiley, **1997**, and cited references.

[32] a) H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, F. Sommer, B. v. Issendorff, *Nature* **2000**, *407*, 60; b) H. Prinzbach, F. Wahl, A.

Weiler, P. Landenberger, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, B. v. Issendorff, *Chem. Eur. J.* **2006**, *12*, 6268.
[33] The first *cis*-tris-σ-homobenzenes, zero-bridged and obtained through [2π + 2σ] photocycloaddition, indeed proved to be thermally rather labile yet preferred to isomerize along a two-step 2σ→2π rather than the symmetry-allowed concerted 3σ→3π pathway; a) an early mechanistic discussion was given in H. Prinzbach, D. Stusche, J. Markert, H.-H. Limbach, *Chem. Ber.* **1976**, *109*, 3505.
[34] a) R. Schwesinger, H. Prinzbach, *Angew. Chem.* **1972**, *84*, 990; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 942; b) R. Schwesinger, H. Fritz, H. Prinzbach, *Chem. Ber.* **1979**, *112*, 3317, and cited references; for the *trans*-trioxide see: c) R. Keller, R. Schwesinger, W. Fritsche, H.-W. Schneider, D. Hunkler, H. Prinzbach, *Chem. Ber.* **1979**, *112*, 3347, and cited references.
[35] E. Vogel, H.-J. Altenbach, C.-D. Sommerfeld, *Angew. Chem.* **1972**, *84*, 986; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 939.
[36] a) R. Schwesinger, M. Breuninger, B. Gallenkamp, K.-H. Müller, D. Hunkler, *Chem. Ber.* **1980**, *113*, 3127.
[37] a) S. Kagabu, H. Prinzbach, *Angew. Chem.* **1975**, *87*, 248; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 252; b) S. Kagabu, C. Kaiser, R. Keller, P. G. Becker, K.-H. Müller, L. Knothe, G. Rihs, H. Prinzbach, *Chem. Ber.* **1988**, *121*, 741.
[38] a) G. McMullen, G. Sedelmeier, R. Hildebrandt, H. Fritz, H. Prinzbach, *Tetrahedron Lett.* **1979**, *20*, 3847; b) H. Prinzbach, H.-P. Schal, D. Hunkler, H. Fritz, *Angew. Chem.* **1980**, *92*, 248; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 567; c) G. McMullen, M. Lutterbeck, H. Fritz, H. Prinzbach, C. Krieger, *Isr. J. Chem.* **1982**, *22*, 19; d) M. Maas, M. Lutterbeck, D. Hunkler, H. Prinzbach, *Tetrahedron Lett.* **1983**, *24*, 2143.
[39] Cf. *Three-membered Ring-Based Molecular Architecture* in: A. de Meijere, S. I. Kozhushkov, H. Schill, *Chem. Rev.* **2006**, *106*, 4926.
[40] a) H. Prinzbach, H.-P. Böhm, S. Kagabu, V. Wessely, H. V. Rivera, *Tetrahedron Lett.* **1978**, *19*, 1243; b) B. Zipperer, K.-H. Müller, B. Gallenkamp, R. Hildebrandt, M. Fletschinger, D. Burger, M. Pillat, D. Hunkler, L. Knothe, H. Fritz, H. Prinzbach, *Chem. Ber.* **1988**, *121*, 757, and cited references.
[41] E.g. Heterodiademanes: D.-R. Handreck, D. Hunkler, H. Prinzbach, *Angew. Chem.* **1989**, *101*, 1386; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1351, and cited references.
[42] a) A. de Meijere, D. Kaufmann, O. Schallner, *Angew. Chem.* **1971**, *83*, 404; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 417; b) J. C. Walton, A. de Meijere, in Houben–Weyl, 4th Ed., Vol. *E17c* (Ed.: E. Schaumann), Thieme, Stuttgart, **1998**, p. 2667 ff; c) A. de Meijere, C.-H. Lee, B. Bengtson, E. Pohl, S. L. Koshuskov, P. R. Schreiner, R. Boese, T. Haumann, *Chem. Eur. J.* **2003**, *9*, 5481, and cited references.
[43] E. g. H. Prinzbach, V. Wessely, H. Fritz, *Tetrahedron Lett.* **1976**, *17*, 2765.
[44] a) W. Seppelt, C. Rücker, C. Kaiser, H. Prinzbach, *Chem. Ber.* **1984**, *117*, 1834, and cited references.
[45] K. Himmeldirk, H.-J. Altenbach, *1,4,7-Triheteronines/1,4-Diheterocines* in Houben–Weyl, 4th ed., vol. E9d (Ed.: E. Schaumann), Thieme, Stuttgart, **1998**, p. 573, 529, 563.
[46] a) D. Sawicka, S. Wilsey, K. N. Houk, *J. Am. Chem. Soc.* **1999**, *121*, 864; b) D. Sawicka, K. N. Houk, *J. Mol. Model.* **2000**, *6*, 158.
[47] H. Prinzbach, *Homobenzenoid Transition States in σ→π Isomerization Reactions*, ISNA III, San Francisco, **1977**.
[48] M. Breuninger, R. Schwesinger, B. Gallenkamp, K.-H. Müller, H. Fritz, D. Hunkler, H. Prinzbach, *Chem. Ber.* **1980**, *113*, 3161, and cited references. For the X,Y = O case see H.-J. Altenbach, E. Vogel, *Angew. Chem.* **1972**, *84*, 985; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 937.
[49] a) K.-H. Müller, C. Kaiser, M. Pillat, B. Zipperer, M. Froom, H. Fritz, D. Hunkler, H. Prinzbach, *Chem. Ber.* **1983**, *116*, 2492; b) B. Zipperer, D. Hunkler, H. Fritz, G. Rihs, H. Prinzbach, *Angew. Chem.* **1984**, *96*, 296; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 309, and cited references.
[50] M. Fletschinger, B. Zipperer, H. Fritz, H. Prinzbach, *Tetrahedron Lett.* **1987**, *28*, 2517.
[51] K. H. Doxsee, *Eight-membered Rings with Two Heteroatoms 1,4* in *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), vol. 9 (Ed.: G. R. Newkome), Pergamon, **1996**, p. 527 ff.
[52] A novel, characteristic structural feature of the tris-σ-homobenzenes **A** was their planar cyclohexane ring as early documented in the X-ray structural analyses for X,Y,Z = O: W. Littke, U. Drück, *Angew. Chem.* **1974**, *86*, 537; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 539; X,Y,Z = NR: W. Littke, U. Drück, *Acta Crystallogr., Sect. B* **1979**, *35*, 1905; X,Y,Z = CHR: ref.[10b] cf. H. Dodziuk, M. Ostrowski, *Eur. J. Org. Chem.* **2006**, 5231.
[53] a) R. Schwesinger, K. Piontek, W. Littke, H. Prinzbach, *Tetrahedron Lett.* **1985**, *26*, 1201; b) R. Schwesinger, K. Piontek, W. Littke, H. Prinzbach, *Angew. Chem.* **1985**, *97*, 344; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 318; c) G. J. Grant, C. D. Grant, W. N. Setzer, *Inorg. Chem.* **1991**, *30*, 354; d) Chaudhuri, K. Wieghardt in *Progress in Inorganic Chemistry* (Ed.: S. J. Lipphard), Wiley, New York, **1987**, p. 336.
[54] a) C. Rücker, H. Prinzbach, H. Irngartinger, R. Jahn, H. Rodewald, *Tetrahedron Lett.* **1986**, *27*, 1565; b) B. Trupp, H. Fritz, H. Prinzbach, *Angew. Chem.* **1989**, *101*, 1381; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1345; c) B. Trupp, D.-R. Handreck, H.-P. Böhm, L. Knothe, H. Fritz, H. Prinzbach, *Chem. Ber.* **1991**, *124*, 1757.
[55] a) W. Fritsche-Lang, P. Wilharm, E. Hädicke, H. Fritz, H. Prinzbach, *Chem. Ber.* **1985**, *118*, 2044; b) R. Gleiter, C. Sigwart, H. Irngartinger, S. Gries, W. Marterer, O. Klingler, H. Prinzbach, *Tetrahedron Lett.* **1988**, *29*, 185; c) H. Irngartinger, D. Kallfaß, H. Prinzbach, O. Klingler, *Chem. Ber.* **1989**, *122*, 175, and cited references.
[56] E. g; a) (2-Desoxy)streptamines: R. Schwesinger, H. Prinzbach, *Angew. Chem.* **1975**, *87*, 625; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 630; H. Prinzbach, R. Keller, R. Schwesinger, *Angew. Chem.* **1975**, *87*, 626; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 632; R. Schwesinger, W. Fritsche, H. Prinzbach, *Chem. Ber.* **1982**, *115*, 946; b) *cis*-1,3(1,4)-(Deoxy)inosadiamines: J. Schubert, R. Keller, R. Schwesinger, H. Prinzbach, *Chem. Ber.* **1983**, *116*, 2524; R. Kühlmeyer, R. Keller, R. Schwesinger, T. Netscher, H. Fritz, H. Prinzbach, *Chem. Ber.* **1984**, *117*, 1765, and cited references; c) Sannamine/sporamine building blocks: B. Seitz, R. Kühlmeyer, T. Weller, W. Meier, C. Ludin, R. Schwesinger, L. Knothe, H. Prinzbach, *Chem. Ber.* **1989**, *122*, 1745; d) (–)-Conduramine E: D. Spielvogel, J. Kammerer, M. Keller, H. Prinzbach, *Tetrahedron Lett.* **2000**, *41*, 7863.
[57] E.g; a) C. Ludin, T. Weller, B. Seitz, W. Meier, S. Erbeck, C. Hoenke, R. Krieger, M. Keller, L. Knothe, K. Pelz, A. Wittmer, H. Prinzbach, *Liebigs Ann.* **1995**, 291; b) S. Erbeck, X. Liang, D. Hunkler, R. Krieger, H. Prinzbach, *Eur. J. Org. Chem.* **1998**, 1935, and cited references.

Received: May 2, 2007
Published Online: August 28, 2007

