The Pagodane Route to Dodecahedranes Unsaturated (Hyperstable) and Saturated Bissecododecahedranes☆

Bulusu A. R. C. Murty, Rolf Pinkos, Paul R. Spurr, Wolf-Dieter Fessner, Georg Lutz, Hans Fritz, Dieter Hunkler, and Horst Prinzbach*

Chemisches Laboratorium der Universität Freiburg i.Br., Institut für Organische Chemie und Biochemie, Albertstraße 21, W-7800 Freiburg, F.R.G.

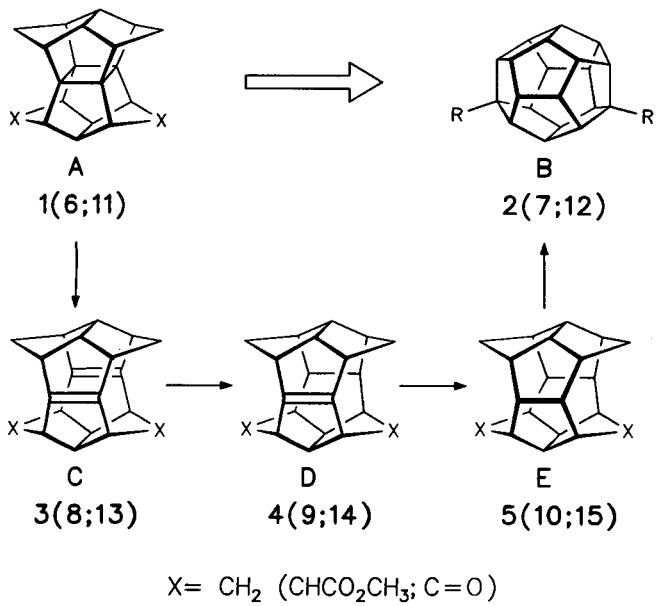
Received February 3, 1992

Key Words: Bissecododecahedranes, saturated, unsaturated / Homoconjugation / Hyperstability / Addition reactions / Cage effects

In bissecododecahedra-1,10(11)-dienes, the *syn*-periplanar and unusually proximate arrangement of the π bonds is responsible for extraordinary physical properties such as strong through-space homoconjugation, low oxidation potentials, and a special reactivity pattern. In pursuit of route B to dodecahedranes[1], the hyperstability predicted (MM2) for these bissecodienes and the related monoenes has been experimentally verified only for the latter in their resistance towards catalytic hydrogenation. Non-hydrogenative saturation of (3,8-difunctionalized) bissecodienes (**3**, **8**, **13**) and monoenes (**4**, **9**, **14**) becomes increasingly hampered due to the increased steric congestion on the more spherical molecular surfaces but can be achieved in "high-driving-force" reactions [*cis*-hydroxylation (**26**, **27**, **41**, **42**), epoxidation (**38**, **54**, **57**, **58**, **60**, **63**, **80**, **83**), cyclopropanation (**55**, **59**, **61**, **64**)]. In contrast, cycloadditive four-, five- (**73**), and six-membered (**76**) ring annulation again is limited to monoadditions. The half-cages in the bissecododecahedrane structures provide for remarkable steric steering and protection [e.g. *anti*-selective protonation (alkylation) of carbanions **57a** (**84a**)$^{2-}$, lack of hydrazone formation from ketones **58**, **89**, resistance of *syn*-bis(acid chloride) **86** towards hydrolysis.

Among the conceptual alternatives for the transformation of [1.1.1.1]pagodanes **A** into pentagonal dodecahedranes **B**, the stepwise B-route (Scheme 1, **A** → **C** → **D** → **E** → **B**) holds the highest promise for broad preparative utilization[1]. In the first step, the 2σ → 2π isomerization of pagodanes **A** to bissecododecahedradienes **C**, a protocol employing bromine addition/elimination, not only proved highly efficient but also applicable to variously functionalized substrates. The dienes **C** available in this way (X inter alia = CH_2, $CHCO_2CH_3$, CHCl, C=O), apart from serving as intermediates in our synthetic scheme, are attractive as homoconjugated dienes of a very special nature[2]. In this paper, we will start with an account of relevant physical and chemical properties of the dienes **C**, as represented by parent diene **3**, *syn,syn*-diester **8** and dione **13** and then detail the pitfalls and difficulties encountered during the pursuit of route B and outline some of the ways for their circumvention.

Scheme 1

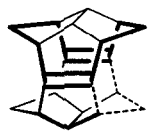


Homoconjugation – Oxidation – Photocycloaddition

Architecturally, the bissecododecahedradiene skeleton **C** is extraordinary insofar as the two tetrasubstituted bridgehead C,C double bonds are locked into a rigid framework where they are perfectly *syn*-periplanar and held at an unusually close proximity. Appropriate dissection of the decacyclic carbon skeleton reveals these double bonds as part of bicyclo[3.3.0]oct-1(5)-ene or of conformationally immobile [*Z*,*Z*(*E*,*E*)]-1,6-cyclodecadiene, [*Z*,*Z*(*E*,*E*)]-1,6-cycloundecadiene, and (*E*,*E*)-1,7-cyclododecadiene rings. The additional transannular bridging of these subunits introduces significant strain into compounds **C** as inter alia manifested in the considerable pyramidalization of the olefinic carbons (ca. 10°)[3,4].

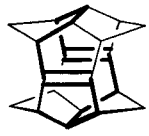
The transannular π,π distance in dienes **C** with calculated 2.63 Å (MM2) for parent diene **3** – probably somewhat too short by a small margin[1] – is unusually short. Concomitant strong through-space π,π overlap causes the relatively long-wavelength charge transfer (c.t.) absorptions as revealed

  0009–2940/92/0707–1719 $ 3.50+.25/0



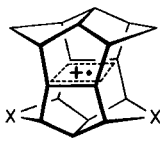
Z,Z(E,E)–deco-

Z,Z(E,E)–undeca-

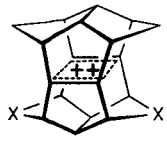


E,E–dodeca–diene

in the UV spectra of these dienes[1,2]. Specifically, the PE (Martin et al.)[5], ESR (Gerson et al.)[6], electrochemical (Heinze et al.)[6], and superacid studies (Olah et al.)[7] – detailed accounts have been or will be presented separately – contribute to a better understanding of some rather perceptive reactivity phenomena, some of which will be described below. Thus, it was learned that the through-space, homoconjugative transannular interaction in dienes **C** (π,π split of 1.9 eV for **3** and even 2.2 eV for dienedione **13**) is unique in that it approximates the conjugation in 1,3-dienes (2.46 eV for 1,3-butadiene) and that there is a high propensity for one- and two-electron oxidations. The resultant transannularly delocalized radical cations **F** and dications **G** are the same stable species observed before in analogous oxidations of pagodanes **A**. The reversible half-wave oxidation potentials with $E_{1/2}$ = 0.66 V for **3** and $E_{1/2}$ = 1.24 V for dienedione **13** [vs. Ag/AgCl in CH_2Cl_2 (SO_2)][6,8] are consequently very low.



F

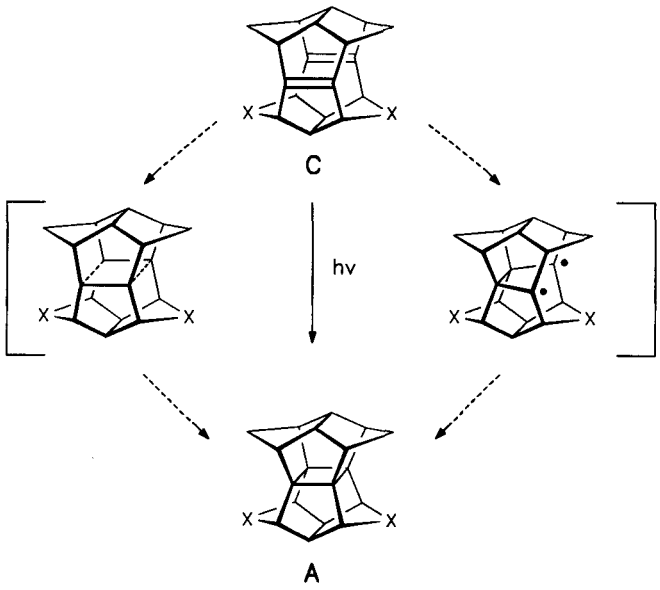


G

X=CH_2 ; $(CH_2)_2$

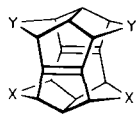
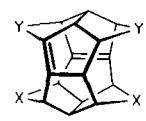
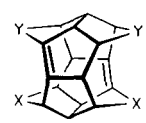
Regarding stereoelectronic and energetic aspects[9], the dienes **C** are ideally set up for intramolecular [$_\pi2_s$ + $_\pi2_s$]-photocyclization[12]. This would lead back to the respective pagodane precursors and thus is only of cursory preparative interest. The reactions have been performed primarily as a reference for preparatively more attractive transformations in related (seco)dodecahedradienes. Referring also to extensive studies with the "molecular halves"[10,11], it suffices here to state that in the three cases studied (**3**, **8**, **13**), direct irradiation, taking advantage of the c.t. absorptions, or preferably sensitized (acetone) excitation selectively, if not uniformly, produces the [2 + 2] cycloadducts (pagodanes **1**, **6**, **11**). There is obviously no competitive pathway available to the conformationally rigid (triplet) diradical intermediates[13].

In this context, a comparison of the calculated (MM2)[14] energies for **3** with those of its isomers which are formally derived by 1,3-hydrogen migration is instructive (Table 1)[15]. The 18.8 kcal/mol enthalpy gap to the closest one in energy truly attests the outstanding stability of **3** ("*anti*-Bredt protection"[16]). Indeed, under no set of experimental conditions could isomerization of **3** to any of those isomers be detected[1]. As was first noted in the superacid experiments with

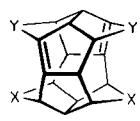
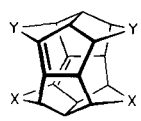
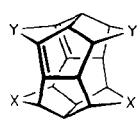


the [2.2.1.1]pagodanes **A** (X = CH_2CH_2)[7], the situation is remarkably different for the corresponding [2.2.1.1] dienes **C** (X = CH_2CH_2), the energies of which are given for comparison in Table 1. Thus, for the derived [2.2.1.1] ions of type **F**/**G** (X = CH_2CH_2) a kinetically as well as thermodynamically clearly more feasible stabilization pathway exists with the deprotonation of the rather acidic[17] bridgehead hydrogens[18] of the [2.2] structural moiety. It should be recalled that attempts directed at the preparation of the [2.2.1.1] dienes had failed because of the contrasting behavior of the [2.2.1.1]pagodane skeletons in the bromination step[1].

Table 1. Calculated energies (MM2) for isomeric [1.1.1.1] and [2.2.1.1] dienes **C**

				
X=Y=CH_2	$\Delta H_f°$	62.0	80.8	93.4
	E_{Str}	73.9	92.8	105.5
X=$(CH_2)_2$,Y=CH_2	$\Delta H_f°$	59.2	75.8	81.7
	E_{Str}	82.6	99.3	105.4

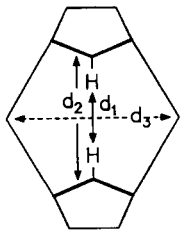
(kcal/mol)

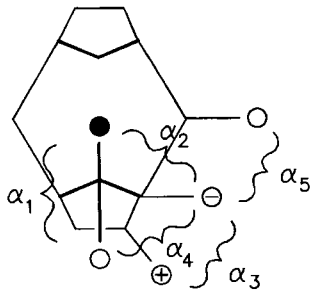
				
X=Y=CH_2	$\Delta H_f°$	94.8	100.4	101.2
	E_{Str}	106.9	112.5	113.3
X=$(CH_2)_2$;Y=CH_2	$\Delta H_f°$	88.2 (77.7)	85.9	95.7 (86.1)
(Y=$(CH_2)_2$;X=CH_2)	E_{Str}	111.8 (101.3)	109.5	119.8 (109.7)

(kcal/mol)

Hyperstability as a Hurdle on Route B to Dodecahedranes

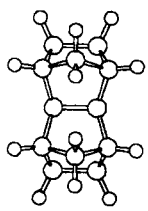
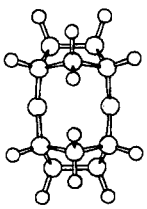
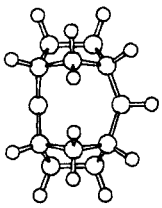
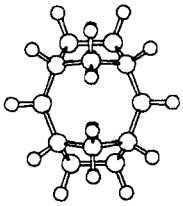
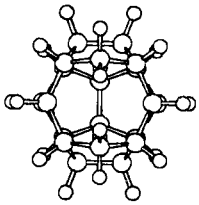
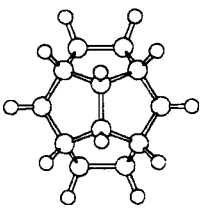
Principally, the saturation of bissecodienes **C** to bissecododecahedranes **E** via bissecoenes **D** enforces essential structural modifications. Specifically, it is the shorter distances between opposing methylene carbons that are considered helpful, if not essential, for the ensuing dehydrocyclizations **E** → **B** (cf. Schemes 1 and 2 in ref.[1]). For the parent bissecodiene **3**, the structural consequences of hydrogenation to **4** and **5** are illustrated in Table 2 (as references, the other members of route **B** are displayed also). From these side views, it can easily be recognized how the increasingly spherical geometry causes progressive vicinal and transannular hydrogen contacts. It is the latter which make up a good part of the "olefin strain" (*OS*)[18] of −11.4 kcal/mol for **3** and of −13.9 kcal/mol for **4** and somewhat reduced with −10.1 (−10.6) kcal/mol for diones **13** and **14**. Correspondingly, the enthalpies of hydrogenation amount only to 12.6/10.1 kcal/mol for **3** → **4**/**4** → **5** and to 13.8/13.3 kcal/mol for **13** → **14**/**14** → **15** as compared to the ca. 26 kcal/mol for tetramethylethylene. As stressed earlier[1], in the force-field calculations the significant transannular π,π destabilization in dienes **C** (**3**, **13**) is neglected with the consequence that the ΔH_f° values are too low and the *OS* values too large by roughly 4−7 kcal/mol. In short, complications with the hydrogenations **C** → **D**, and more so for that of **D** → **E**, should not be too surprising.





Exemplary results of a series of hydrogenation runs are listed in Table 3. Hydrogenation of **3** indeed occurred relatively rapidly and provided uniformly monoene **4**. The latter proved to be truly hyperstable; even under extreme conditions, not even trace amounts of **5** could be detected (TLC, GC, ^{1}H NMR). In the product mixtures, containing **1**, **3**, and **4**, the secopagodane **17**[1] was notoriously an important if not dominant component. In reactions of **4** at higher temperatures, even under very high hydrogen pressure, dehydrogenation to **3** prevailed (cf. the temperature dependence in the debromination step leading to **3**[1]). In a number of experiments employing **3**(**4**) and other catalyst systems (Pt, Rh) under process conditions that provide "hydrogen-rich catalysts", again no **5** was found in product mixtures that were similar in composition to those given in Table 3. Hydrogen abstraction in **4** to furnish the stabilized homocon-

Table 2. Changes in calculated transannular distances [Å] and H,H geminal/vicinal interplanary angles [°] along route B (MM2, in parentheses MM3)

	 **1**	 **3**	 **4**	 **5**		 **2**
d_1:	2.26 (2.24)	1.98 (1.89)	1.93 (1.82)	1.87 (1.73)	1.89 (1.79)	-
d_2:	3.50 (3.50)	3.21 (3.21)	3.14 (3.14)	3.02 (3.01)	3.04 (3.12)	1.53 (1.54)
d_3: (Å)	1.54 (1.58)	2.62 (2.62)	2.98 (2.99)	3.47 (3.50)	3.89/ (3.82/ 3.60 3.45)	4.00 (4.04)
α_1:	109.9 (109.4)	105.7 (106.4)	104.5 (105.6)	101.9 (104.0)	102.5 (105.0)	
α_2:	64.3 (63.1)	52.4 (50.3) 41.9 40.0)	52.6/ (50.5/	40.5 (38.6)	37.5 (35.5)	0 (0)
α_3:	61.0 (61.2)	65.8 (68.5)	63.8/ (67.2/ 75.3 77.8)	72.7 (76.9)	76.4 (81.7)	
α_4:	41.8 (38.9)	29.9 (27.5)	30.9/ (29.0/ 18.7 17.6)	17.6 (17.1)	15.4 (15.1)	0 (0)
α_5 : (°)			1.6 (0.0)	1.1 (0.5) 5.4 6.7)	7.8/ (7.5/	0 (0)

jugated radical **16** generally seems to be the kinetically dominating pathway[19]. Ionic chain hydrogenation, as is often successfully applied to tetraalkyl olefins[20], was excluded because of the acid sensitivity of **3** and **4**.

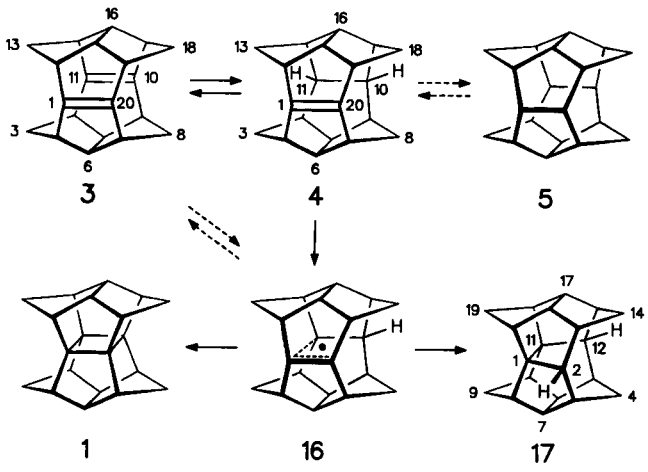


Table 3. Product distribution in exemplary hydrogenation experiments with **3** and **4** (r.t. = room temperature)

3: Pd/C (10%)	1 atm H_2, 3h, r.t. :	95% **4**
	200 atm H_2, 24h, r.t. :	15% **1**, 26% **3**, 11% **4**, 52% **17**
4: Pd/C (10%)	100 atm H_2, 8h, 80 C:	54% **3**, 41% **4**, 5% **17**

Tetrasubstituted C,C double bonds are known to be hydrogenated by diimide[21]. The early and sterically relatively undemanding transition states as suggested for these four-center reactions[22] were considered helpful to overrule the hyperstable situation.

When diene **3** in ethanol/THF solution was exposed to excess N_2H_2 (up to 50 equivalents) at room temperature, careful GC/MS analysis revealed the exclusive and quantitative formation of monoene **4**. On the 100-mg scale, the solid residue isolated by extractive workup is pure **4**; in runs on the g scale (85% av. yield) some material is probably lost due to partial oxidation and polymerization occurring during the isolation procedure. In fact, when exposed to air, **4**, like diene **3**, decomposed into oxygenated monomers (i.a. epoxide **60**) and polymers. It therefore should be handled in an inert atomsphere.

The m.p. of **4** was found to be identical to that of **17** (333 °C). Indeed, upon heating (probably with no total exclusion of air) **4** cleanly isomerized to **17**. The C=C stretching frequency of 1649 cm^{-1} in the Raman spectrum of **4** is higher by 24 cm^{-1} than that measured for the (less strained) diene **3** (1625 cm^{-1})[1]. Compared with the latter (Figure 3 in ref.[1]), in the ^1H- and ^{13}C-NMR spectra of **4** (Figure 1), measured in [D_6]benzene for better resolution, the signal for the now closer *syn*-methylene hydrogen atoms is shifted downfield (by 0.29 ppm), whereas the signal for the more pyramidalized, transannularly non-conjugated olefinic carbon atoms is shifted upfield (by 3.9 ppm). The newly introduced 10(11)-hydrogens are nearly eclipsed with their neighboring hydrogens [α_5 = 1.6(0.0)°] and thus give rise to the lowest signal (δ = 3.10). In line with the respective calculated dihedral H,H angles, the measured vicinal H,H coupling constants on the more spherical, saturated side are typically larger ($J_{3a,4}$ = 6.5 Hz) than on the unsaturated side ($J_{2,3a}$ = 4.5 Hz).

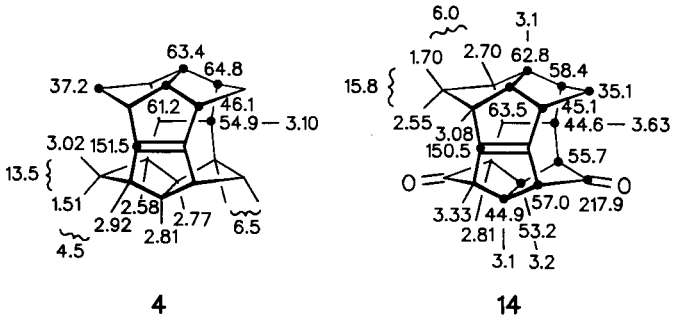
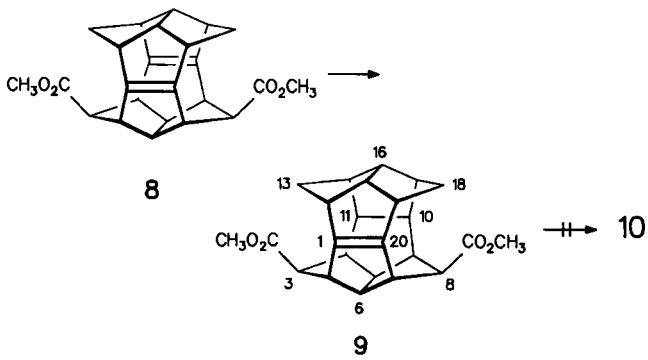
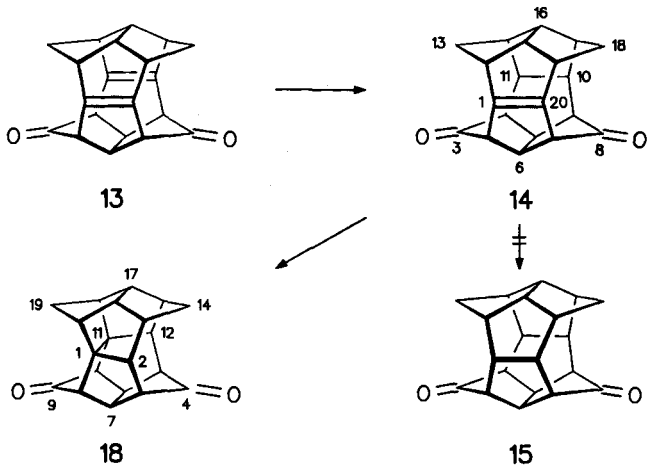


Figure 1. ^1H- and ^{13}C-NMR data [δ, J (Hz)] of bissecoene **4** (C_6D_6) and bissecoenedione **14** ($CDCl_3$)

In the case of *syn,syn*-diene diester **8**, obstruction by the ester functions even to the first hydrogenation step, due to increased transannular/torsional strain, seemed not improbable. Yet, diimide (large excess) reduced **8** rapidly and specifically (95%) to the monoene **9** with no trace of **10** being detected by GC/MS. In the completely assigned ^1H-NMR spectrum of **9**, the 13(18)*s*-H signal appeared at rather high field (δ = 2.04; J = 14.4 Hz; $CDCl_3$) in line with the opposing, perpendicularly fixed CO_2R groups exerting a shielding influence.



Bissecododecahedranedione **15** was and still is valued as a promising precursor for variously functionalized dodecahedranes. In the sequence of diones **13** → **14** → **15**, strain increase in as much as it is caused by transannular and vicinal H/H interactions is smaller than for the analogous hydrocarbons (Scheme 2 in ref.[1]). We therefore hoped that total saturation of **13**, if not by catalytic then by diimide hydrogenation, would have better prospects than for **3**. Yet, with a broad range of catalytic hydrogenation conditions, no **15** was found in generally rather complex product



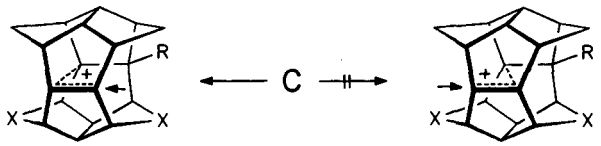
mixtures consisting mainly of monoene **14**. With diimide, too, only monosaturation **13** → **14** was observed. The course of the reaction was unaffected by higher reaction temperatures[22], as slow generation of diimide from decomposition of *p*-tosylhydrazine (excess) in refluxing diglyme in the presence of catalytic amounts of pyridinium tosylate again yielded only **14**: no hydrazone of any type was discovered (vide infra). Filtration through silica gel with exclusion of air is sufficient to obtain pure **14** (89%). As in the case of **4**, even under persuasive conditions (e.g. 5% Rh/Al_2O_3, EtOAc, 20 atm H_2, 100°C, 16 h), catalytic hydrogenation **14** → **15** could not be brought about and instead only slow decomposition was observed. On heating to 330°C (15 min), **14** cleanly underwent the same type of rearrangement already noted for **4** to provide the more stable secopagodanedione **18**.

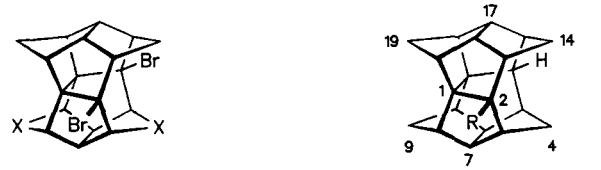
By a comparison of the ^1H- and ^{13}C-NMR spectra of **14** (Figure 1) with that of **13** (≡ **11** in Figure 4 in ref.[1]) and of the pair **3**/**4**, a slightly larger chemical shift for the 13(18)*s*-H and a somewhat smaller shift for the olefinic carbon atoms ($\Delta\delta$ = 10.7) are noted. Structure **18** rests on the completely assigned ^1H-NMR spectrum (i.a. $J_{2,3} = J_{2,15} = 9.7$; $J_{14a,14s} = 14.7$; $J_{19a,19s} = 11.2$ Hz) and the comparison with that of the parent hydrocarbon (cf. **7** in Figure 2 in ref.[1]).

The question remains, why in spite of comparable changes in strain the rates for the two hydrogenation steps **C** → **D** and **D** → **E** are generally so much different. It should be recalled, though, that within a series of cycloalkanes no correlation between the relative hydrogenation rates and ground-state strain energies or differences between reactant and product strain had been found[22–24]. A reasonable ad hoc explanation for the higher reactivity of the dienes **C** (**3**, **8**, **13**) invokes a considerable driving force arising from the strong through-space π,π destabilization. Yet, whenever this antibonding situation is changed to a stabilizing one, a high propensity for transannular bond formation is noted (as in the thermal isomerizations **4** → **17** and **14** → **18**) via presumably homoconjugated radicals of type **16** (cf. **H**, **I**).

Transannular Additions

Directly related to the special architecture of the dienes **C** and to the nature of the resultant homoconjugative interactions is the course taken in the "charge-controlled" addition of electrophiles. Of the two potential transannular addition modes, via homoconjugated cations **H** and **I**, only the former is operating. In an exploratory study including dienes **3**, **8**, and **13** and various electrophiles (Br_2, HCl, HOAc, H_2O/H^+, BH_3), rapid and regiospecific homoconjugative addition to form the secopagodanes **19**–**25** was observed. As exemplary cases, the addition of bromine to **3** and **13** to give the precursor dibromides **19** and **21**[1], respectively, and that of HCl to **3** to give chloride **22** are detailed in the Experimental Section; for comparison, the NMR data of **24** and **25** are also listed there. The skeletal rigidity clearly prohibits the structural adjustment which would be required for the addition mode **I** to compete. This latter mode is observed often in more flexible bridgehead cyclodienes[25].





	19	20	21
X	CH_2	$CHCO_2CH_3$	CO

	22	23	24	25
R	Cl	Br	OH	$OCOC_6H_4Cl$(m)

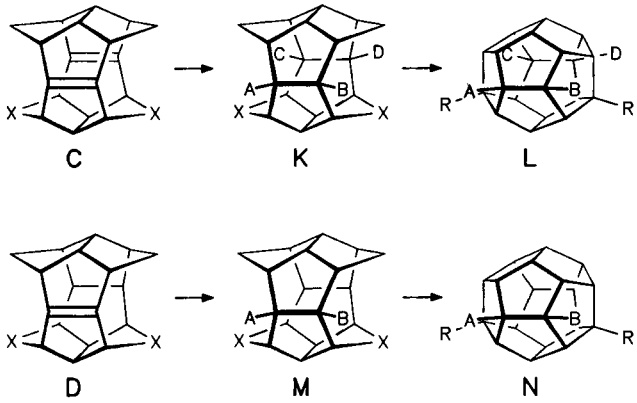
Vicinal Additions

The resistance of bissecoenes **D** to be hydrogenated to the saturated bissecododecahedranes **E** delivered a severe blow to our pagodane → dodecahedrane program in its original version (Scheme 1 in ref.[1]). As will be better understood in view of the details presented in the following paper[26], little hope was seen to obviate this step by bringing about dehydrocyclization already at the stages of the bissecodienes **C** or bissecoenes **D**. The lateral C,C distances (d_2 in Table 2) are rather large and the unsaturated dodecahedranes probably too reactive. In fact, when diene **3** or ene **4** were subjected to the dehydrogenative C–C bond forming conditions successfully used in the Paquette synthesis[27], no monomeric material could be desorbed any more from the catalyst.

Saturation of the **C** and **D** intermediates by other means than hydrogenation (Scheme 2, A–D ≠ H) and by having recourse to reagents which liberate sufficient driving force to overcome the intrinsic strain barriers appeared a prima facie solution of this dilemma. In principle, with functionalities A–D in the bissecododecahedranes **K**/**M**, the original synthetic scheme would be expandable to polyfunctionalized

dodecahedranes **L** and **N** as target structures. The risk that the newly introduced substituents (A – D, R) would not survive the ultimate bond forming processes had to be accepted at this stage. Nevertheless, their (clean) removal would still be useful for the preparation of the much desired, yet still elusive intermediate **5** or, less likely, for opening up a potentially superior access to the parent dodecahedrane **2**[27]. It is implicit, that more voluminous groups A – D would enhance some of the strain factors which qualify **3** and **4** as hyperstable.

Scheme 2



In view of the high propensity of dienes **C** and even of monoenes **D** for transannular bonding via ionic (**H**) or analogous radical-type intermediates, the assortment of methodologies appropriate for their saturation[23] was supposedly restricted to only "concerted"-type, "overlap-controlled" transformations and to neutral or basic reaction conditions.

In the context of the installation of oxygen functionalities into substrates of type **C** and **D**, hydroboration[28] as a well established *syn*-addition is just one of the methodologies eliminated by the above prerequisities. For *cis*-hydroxylation[29] of parent diene **3** as well as for subsequent glycol cleavage reactions[30], the progression in strain is presented in Figure 2[31]. In line with the steric strain introduced by two vicinal OH groups and the angular dependence of the vicinal H/OH steric energy, the increase in strain energy in going from diene **3** to enediol **26** is only slightly larger than that for the hydrogenation **3** → **4**. In going from **26** to tetrol **28**, however, this increase is significantly larger than for the hydrogenation **4** → **5**. It therefore could safely be expected that enediol **26** would only reluctantly undergo further hydroxylation and that it would be at least as hyperstable as monoene **4**. On the other hand, as judged by relative strain energies, **26** as well as the *vic*-diols **27**/**28** were expected to be relatively prone to oxidative cleavage (to **29** – **32**).

Diene **3** reacted rapidly with alkaline $KMnO_4$ (1.2 equivalents) at $-35 \rightarrow 0\,^{\circ}C$ to give a single product (TLC) which was isolated after crystallization from ether in 96% yield. The structural assignment as octacyclic ene dione **29**[32] with its conformationally fixed cyclooctane-1,5-dione subunit[33] was unequivocally established by MS [EI; *m/z* (%) = 292 (10) [M^+], 155 (100)], IR ($\tilde{\nu}_{CO}$ = 1658 cm^{-1}), and the completely assigned ^1H- and ^{13}C-NMR spectra (Figure 3). Attempts to stop the oxidation at the stage of the enediol **26** by varying the reaction conditions (amount of oxidant, pH, temperature) failed. Glycol cleavage, which profits from a

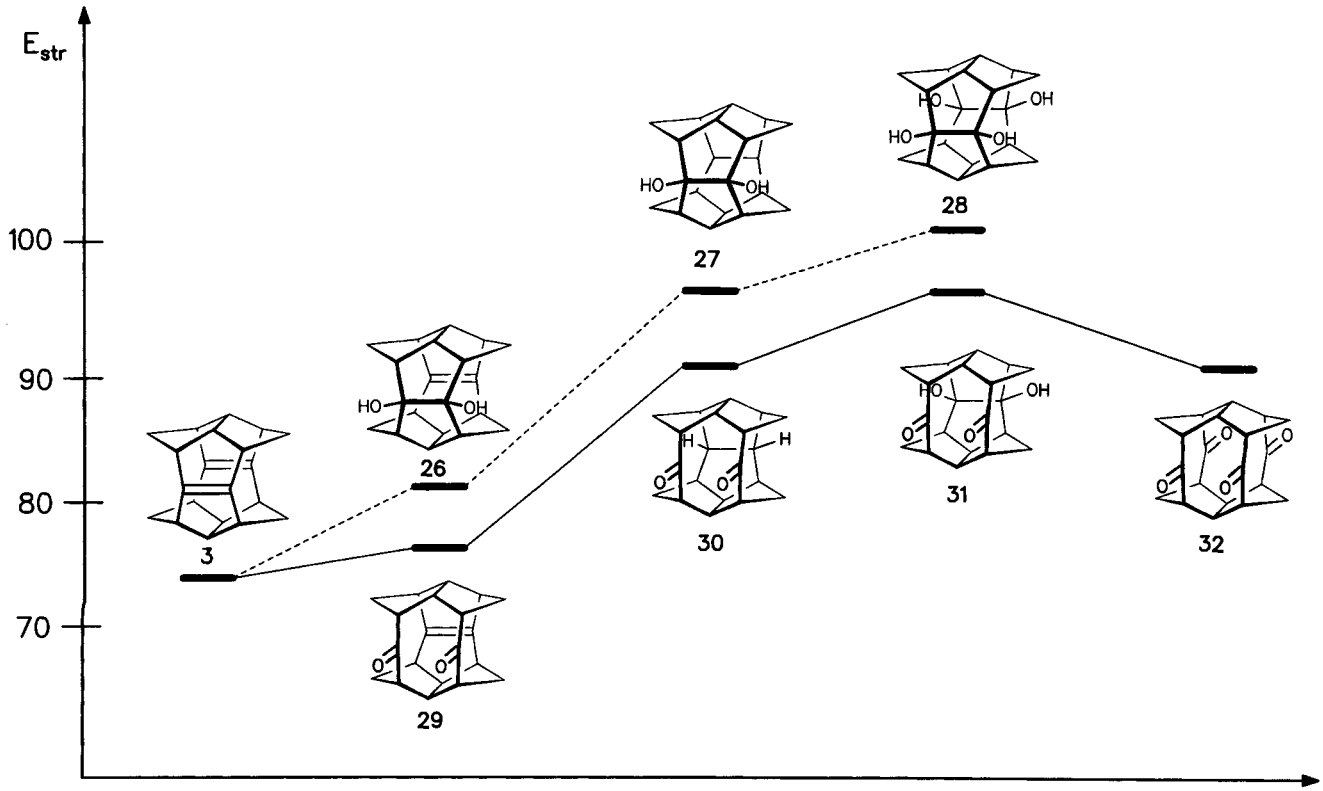
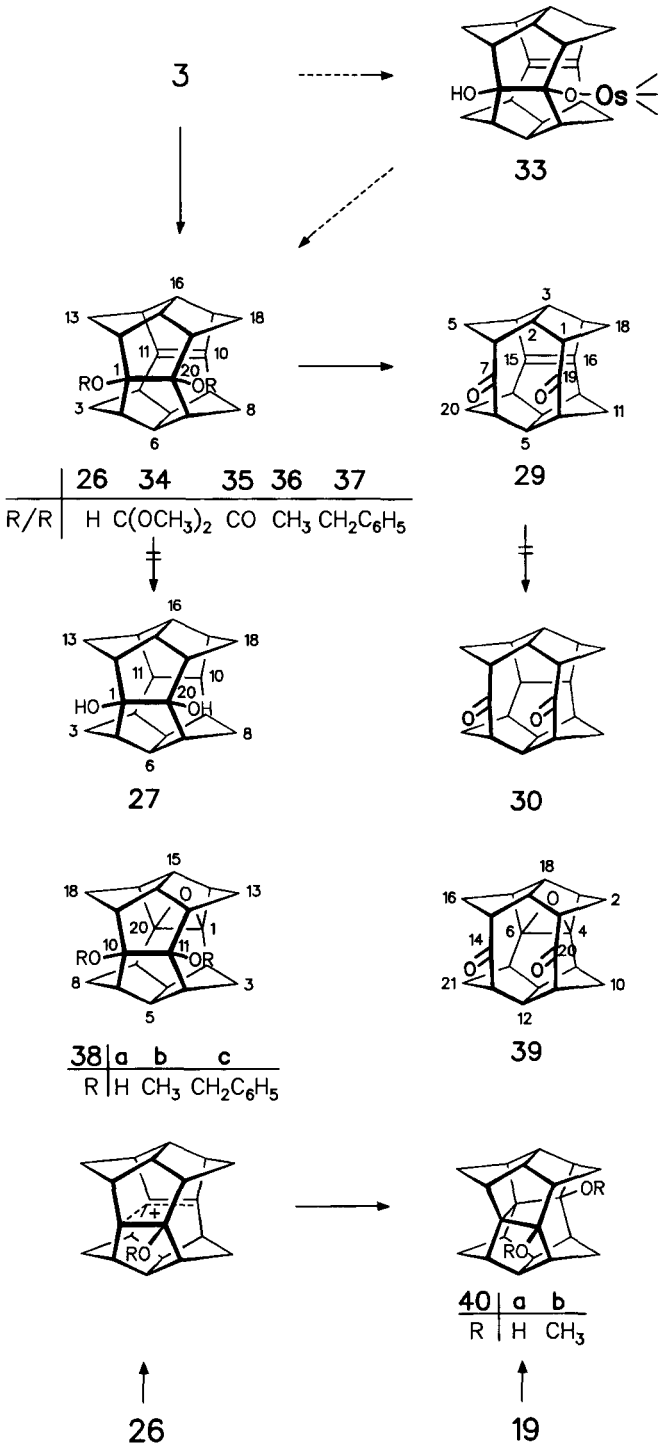


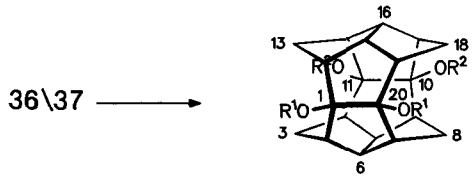
Figure 2. Progression in strain energy (MM2, kcal/mol) for oxidation products of **3** and **4**

gain of ca. 5 kcal/mol in strain energy (Figure 2), in fact was so rapid that **26** could not even be detected in samples taken after partial conversion of **3** at −35°C. On the other hand, rather drastic conditions were needed (dil. HCl, $KMnO_4$, 50°C) to provoke any further oxidation of **29**. However, in the resulting complex mixture of supposedly lactones and hydroperoxides (cf. **52**), neither diol dione **31** (ΔE_{str} = 16.8 kcal/mol) nor tetrone **32** (ΔE_{str} = 11.1 kcal/mol) were present (TLC, ^{1}H-NMR, GC/MS). Mixtures of similar composition also resulted from oxidation experiments with similar strong oxidants proven for critical cases ($RuCl_3/NaIO_4/CCl_4/CH_3CN/H_2O$[34] or RuO_4/CCl_4[35]). Compound **29**, expectedly, turned out to be hyperstable as an excess of diimide did not bring about hydrogenation to **30** (*OS* = −11.3 kcal/mol). On the other hand, standard epoxidation proceeded unbiased to yield epoxydione **39** [96%, m.p. > 350°C; *m/z* (%) = 280 (44) [M^+ − CO]; 55 (100); $\tilde{\nu}_{C=O}$ = 1663 cm^{-1}; $J_{1,19}$ = 11.5; $J_{2a,2s}$ = 15; $J_{2a,3}$ = $J_{3,18}$ = 5.5; $J_{8,12}$ = 11 Hz; $\delta_{C\text{-}4(6)}$ = 82.6; $\delta_{C\text{-}14(20)}$ = 212.4].

Conversely, enediol **26** became conveniently accessible by making use of the insolubility of its osmate half-ester **33** in benzene. When **3** was treated with equimolar amounts of OsO_4 in benzene at room temperature[36], a green-brownish solid deposited quantitatively which proved not to be the C_{2v}-symmetrical cyclic osmate but rather the C_s-symmetrical half-ester **33** (^{1}H NMR). Presumably for steric reasons, **33** resisted scission by Na_2S[37] or transesterification with mannose[38]. Clean reduction to **26**, however, was achieved with $LiAlH_4$; after crystallization from CH_2Cl_2/ether, the yield of **26** was reproducibly higher than 85%. As pointed out above for **4** (Figure 1), the vicinal H,H coupling constants (Figure 3) are distinctly larger on the hydroxylated and more convex side than on the olefinic and more flattened side − in line with the respective (calculated) interplanary angles (cf. Table 2). Upon heating, **26** darkened above 240°C and did not melt below 330°C. Upon acid catalysis, it rapidly isomerized to secopagodanediol **40a**. The latter was independently prepared by hydrolyzing dibromide **19** in wet DMSO (100%) and was derivatized to the known dimethyl ether **40b**[1]. In line with the calculations (*OS* value of −14 kcal/mol), **26** proved hyperstable and could not be hydrogenated by diimide (no **27**). Oxidation by benzoyl peroxycarbamic acid[39] produced quantitatively epoxydiol **38a**. Epoxides **38b, c** were similarly obtained from the corresponding ether/alkyl derivatives of **26** (**36**, **37**). Acid sensitivity of **26** showed up in the reaction with *m*-chloroperbenzoic acid, where the presence of buffers (e.g. $NaHCO_3$) could not prevent the formation of transannularly bound products (i.a. monoester of **40a** with *m*-chloroperbenzoic acid). Similar side reactions complicated the acetalization of **26** with 2,2-dimethoxypropane (to give **34**) and the esterification with phosgene (to give carbonate **35**). In the latter case, these complications could be avoided by using the combination of a BEMP iminophosphorane base [(2-*tert*-butylimino)-2-(diethylamino)-1,3-dimethyl-1,3,2-diazaphosphinane[40]] and trichloroacetyl chloride, where carbonate **35** was obtained in 92% yield. Alkylation of **26** with NaH/CH_3I ($C_6H_5CH_2I$) at room temperature provided the diethers **36** (**37**) (> 90%). *cis*-Hydroxylation of **36** and **37** to yield the dihydroxy diethers **41** (92%) and **42** (88%) was unproblematic. As observed for **26**, alkylation of the OH groups in **41** (**42**) was sterically unfavorable and proceeded slowly (at 20 and 60°C, resp., up to 4 d) but uniformly to provide the tetraethers **43** (94%) and **44** (88%). In the course of the dehydrocyclization experiments[24], it had been demonstrated that tetrol **28** could be regenerated from the tetrabenzyl ether **44** by hydrogenolysis under mild catalytic conditions.

In **41**−**44**, the rather convex bissecododecahedrane skeleton of the so far elusive parent compound **5** is closely ap-





	28	41	42	43	44
R^1	H	H	H	CH_3	$CH_2C_6H_5$
R^2	H	CH_3	$CH_2C_6H_5$	CH_3	$CH_2C_6H_5$

proximated. NMR data for the C_{2v}-symmetrical tetramethyl ether **43** are presented in Figure 3. The geminal H/H coupling constants, nicely reflecting the angle changes at the methylene positions (α_1 in Table 2), are larger than in any of its precursors. A slightly larger down-field shift for the *syn*-methylene hydrogen signal of **43** than for that of **26** is evidence for the decrease in transannular H/H distance as is the $J_{2,6}$ value of 10 Hz for a reduced interplanary angle between these pairs of hydrogens [in **5** = 17.6(17.1)°; Table 2].

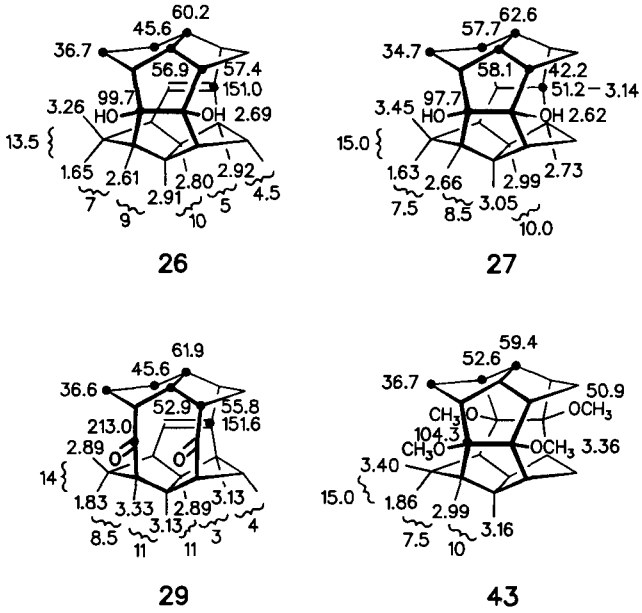
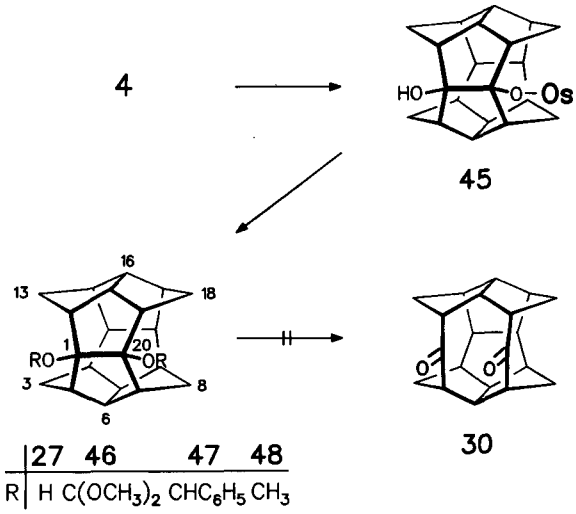
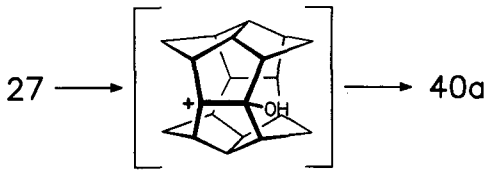


Figure 3. ^{1}H-NMR- and ^{13}C-NMR data of ene diol **26**, diol **27**, ene dione **29**, and tetramethyl ether **43** ($CDCl_3$)

Hyperstable monoene **4** remained inert towards $KMnO_4$ at room temperature under variously modified conditions (KOH, CH_2Cl_2, H_2O, acetone, TEBA-Cl, 18-crown-6/benzene[41]). At higher temperatures (100°C) and with more forcing oxidants ($KMnO_4/NaIO_4$[42], $KMnO_4/SiO_2$[43], Mn_2O_7[44]) only very slowly (days) did a product appear (up to 20%), and this was identified as the secopagodanediol **40a**[1]. With OsO_4 in benzene solution at room temperature, oxidation was still very slow but highly selective (TLC, ^{1}H NMR). For a complete conversion, equimolar amounts of OsO_4 and reaction times amounting to days were needed. As for **33**, the insoluble greenish-brown osmate half-ester **45** was reduced by $LiAlH_4$ to provide the diol **27** which was crystallized from ethyl acetate/CH_2Cl_2 (96%, m.p. > 330°C). Mass (*m/z* (%) = 296 (100) [M^+]) and NMR spectra (Figure 4) ascertained the C_{2v} symmetrical structure. As observed for the related compounds **41**–**44**, the vicinal H/H coupling constants ($J_{2,6}$ = 8.5 Hz) approaching 10 Hz for the strictly eclipsed 5(6)- and 15(16)-hydrogens, attest the high level of skeletal convexity.

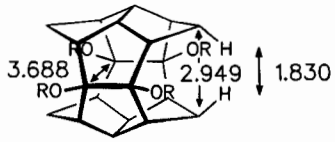


	27	46	47	48
R	H	$C(OCH_3)_2$	CHC_6H_5	CH_3



Though less pronounced than for unsaturated **26**, saturated bissecodiol **27** also showed a high propensity for carbenium ion formation at C-1(20) and thus is also quite acid-sensitive. Exposure to e.g. 2,2-dimethoxypropane or benzaldehyde under slightly acidic conditions did not provide the sterically rather congested acetals **46** or **47** but instead a mixture of secopagodane-type products which were not fully analyzed. Practically quantitative, but slow, was the twofold etherification with NaH/CH_3I at room temperature to provide the crystalline diether **48** in a yield higher than 95%. Attempts to selectively oxidize **27** to dione **30** were fruitless.

For tetrabenzyl ether **44** as a prototype of saturated bissecododecahedranes **E**, crucial structural parameters from an X-ray analysis are shown in Figure 4. A detailed discussion will be presented in a broader context[4]. The enlargement of the pagodane "waist" (d_3) to a transannular C1–C11 (C10–C20) distance of 3.688 Å reduces the lateral C3–C13 (C8–C18) (d_2) and H3–H13 (H8–H18) (d_1) distances to 2.949 and 1.830 Å (av.), respectively [the corresponding calculated (MM2) values for the tetrahydroxy structure **28** are 3.612, 2.973, and 1.864 Å]. Specifically, the experimental transannular distance between the *syn*-methylene hydrogens of 1.830 Å (av.) is considerably smaller than the van der Waals value.

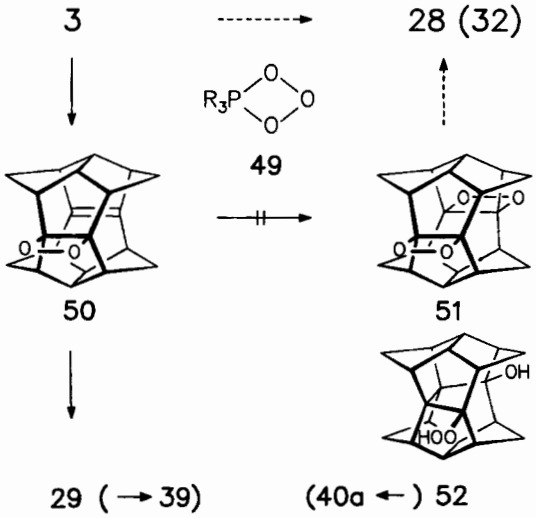


44

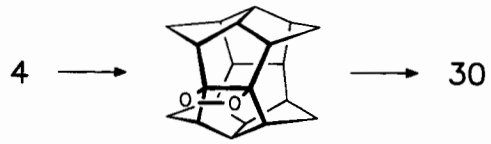
Figure 4. Selected structural data [Å] for tetrabenzyl ether **44**

The bis-1,2-dioxetane **51**[45] constitutes an attractive precursor for tetrol **28**. For several reasons, an ene reaction between **3** and singlet oxygen ($^1O_2$) is unlikely (cf. the 18.8 kcal/mol increase in strain energy from **3** to the closest diene in Table 1), though, the second addition to the mono-dioxetane **50** should have good prospects. A kinetic stability of **50** sufficient to allow the second addition to occur and for **51** to be observable had precedent in the parent tricyclic dioxa[3.3.2]propellane (3,4:3,4-dipropano-1,2-dioxetane) which is isolable in crystalline form and whose thermal cleavage needs an activation energy of 25.6 ± 0.6 kcal/mol[46].

Considering the oxygen sensitivity of diene **3**, it was decided to utilize trioxa phosphetanes as sources of $^1O_2$. In experiments of a more preliminary nature (and therefore not detailed in the Experimental Section), a large excess of the ozonide reagent **49** (R = OC_6H_5) was needed for complete conversion of **3**. By TLC and ^{1}H-NMR monitoring, up to six products in varying percentages were discernible, four of which were separated by chromatography and identified as ene dione **29** (5–15%), epoxy dione **39** (20–35%), secopagodanediol **40a** (20–35%), and the corresponding hydroxy hydroperoxide **52** (20–35%). The failure to observe any tetrone **32** makes the intervention of bisdioxetane **51** highly unlikely as the isomerization **50** → **29** is obviously very fast[44]. It can be speculated whether the transannular bridging to inter alia **40a** or **52** is better explained on the basis of the ene dioxetane **50** or the sterically better adjusted dipolar perepoxide. In control experiments, ene dione **29** proved resistant to treatment with **49** and only with a vast excess of reagent did epoxide **39** emerge as the singular monomeric product besides mainly polymers.



The behavior of hyperstable **4** towards $^1O_2$ is reminiscent of the resistance of **50** (**29**) towards dioxetane formation. Under the conditions applied to **3**, consumption of **4** was very sluggish and required a vast excess of **49** to be complete. The appearance of small amounts (up to 10%) of what is considered to be dione **30** ($\tilde{\nu}_{C=O}$ = 1650 cm^{-1}) besides lactones, hydroperoxides (IR, ^{1}H NMR, GC/MS), and mostly polymers, would suggest that $^1O_2$ addition to **4** (to give **53**) had indeed taken place, if only to a small extent.

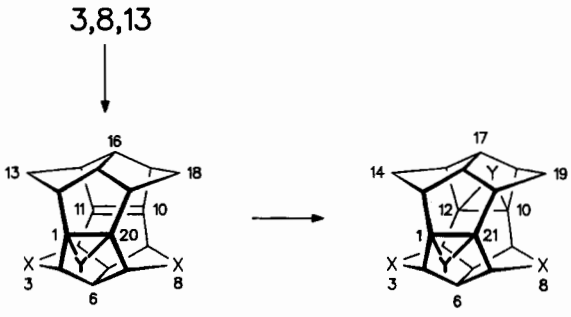


53

Annulation Reactions

Annulation of stable rings (as opposed to e.g. of highly labile 1,2-dioxetanes **50**/**53** or 1,2,3-trioxolanes[47]) to the C=C double bonds of dienes **C** and monoenes **D** was pursued primarily as an alternative method of saturation and hence of better adjusting the respective skeletons to the final lateral dehydrocyclizations (**K**, **M**) while at the same time introducing functionalities (A–D) into the target dodecahedranes **L** and **N**. As such functionalities, either the originally attached rings or fragments derived from them would have been welcomed. Specifically with the attachment of three-membered rings to dienes **C**, the question arose as to whether the ideal coplanar orientation of π and σ (Walsh) orbitals would give rise to measurable, potentially photochemically useful [π_2 + σ_2] or even [σ_2 + σ_2] through-space interactions[5]. As expected from force-field calculations and assessed by X-ray structural data (Figure 6), the replacement of the C=C double bonds in **3** by the C–C bonds of oxirane or cyclopropane rings – in line with the considerable π character[49] – induces relatively small structural changes and places **56** closer to **3** than to **5**.

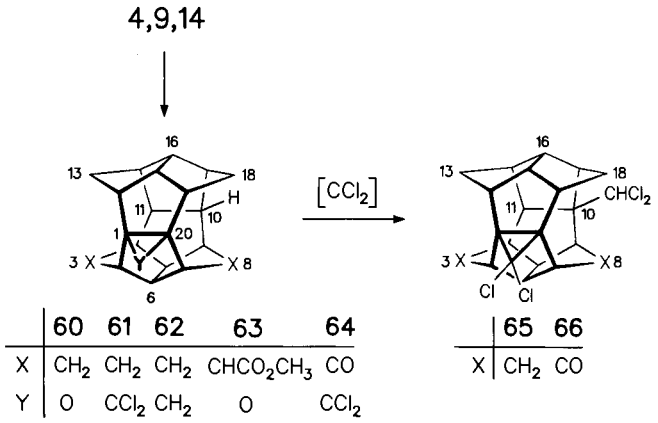
Twofold epoxidation of bissecodienes **3** (**8**, **13**) by peracids, because of the olefin-like, three-center transition state for the concerted oxygen transfer, was expected to hold more promise than twofold hydrogenation by diimide. As for diimide reductions[28], no direct correlation between epoxidation rates and strain energies had been observed within a series of strained olefins[50]. Experimentally, the respective mono- and, to a lesser extent, dioxides were found to be sensitive to acids, in this respect similar to the dienes. Thus, in the oxidation of **3** and **8** with *m*-chloroperbenzoic acid and even more with peracetic acid (even in the presence of buffers) side reactions, e.g. **54** → **40a**, could not completely be avoided. Such complications are well-known for the (*exo*) epoxidation of other proximate dienes (e.g. norbornadi-



	54	55	56	57	58	59
X	CH_2	CH_2	CH_2	$CHCO_2CH_3$	CO	CO
Y	O	CCl_2	CH_2	O	O	CCl_2

ene[51] or isodrin-derived dienes[52]). The use of benzoylperoxycarbamic acid once more provided the solution and with an excess of reagent, the dioxides **54** and **57** became nearly quantitatively accessible. For **13**, the carbonyl functions reduce the acid sensitivity to allow a smooth (95%) transformation into **58** with *m*-chloroperbenzoic acid (NaOAc buffer). In each case, the two epoxidation steps are kinetically not significantly differentiated, so that with one equivalent of peracid (separable) mixtures of diene, mono- and diepoxide are formed.

For the oxidation of monoenes **4** and **9**, benzoylperoxycarbamic acid again was the reagent of choice in that the yields of oxides **60** and **63** came close to 100%. With *m*-chloroperbenzoic acid, the oxidation proceeded beyond **60** and **63** to additionally produce the dioxides **54** and **57** highly regioselectively. The hyperstability of the intermediate ene oxides is a measure of the driving force to bring about dehydrogenation in **60** and **63** at C-10(11). Similar experiences had been reported by Paquette for the epoxidation of a secododecahedrene (with Na_2CrO_4)[53].



	60	61	62	63	64
X	CH_2	CH_2	CH_2	$CHCO_2CH_3$	CO
Y	O	CCl_2	CH_2	O	CCl_2

	65	66
X	CH_2	CO

There was also no kinetic barrier encountered for double cyclopropanation of **3**. Addition of dichlorocarbene under phase-transfer conditions (> 95% **55**) and subsequent dehalogenation of **55** to give **56** (98%) were practically quantitative. In the analogous transformation of **4** to **61** (**62**), the congested C10(11)–H bonds in **61** once more caused a complication – carbene insertion to give **65**[54]. The rate of this latter step was, however, slow enough to allow with one equivalent of $CHCl_3$ the highly selective formation of **61**. With an excess of reagent, **65** could be prepared in 84% yield, and there was no sign of subsequent CCl_2 insertion into the C(11)–H or any other C–H bond. According to NMR evidence, diene dione **13** similarly provided a bisadduct **59** and ene dione **14** a monoadduct **64** which reacted further to **66**.

Most of these homobissecododecahedrane structures are fully confirmed, though some of them only spectroscopically. The ^{1}H- and ^{13}C-NMR spectra (Figure 5) of the prototypes **54** (*m/z* = 292 (100%) [M^+]), **56** (*m/z* = 288 (100%) [M^+]), and **60** (*m/z* = 278 (100%) [M^+]) disclose convincing structural evidence, with the H,H coupling constants and the chemical shift of the *syn*-methylene hydrogen signals as the very qualitative measure of the only limited embulgement of the molecular shapes caused by the newly installed three-membered rings. In **65**, according to the NMR spectra, nonsymmetrical, rotationally hindered conformations are enforced.

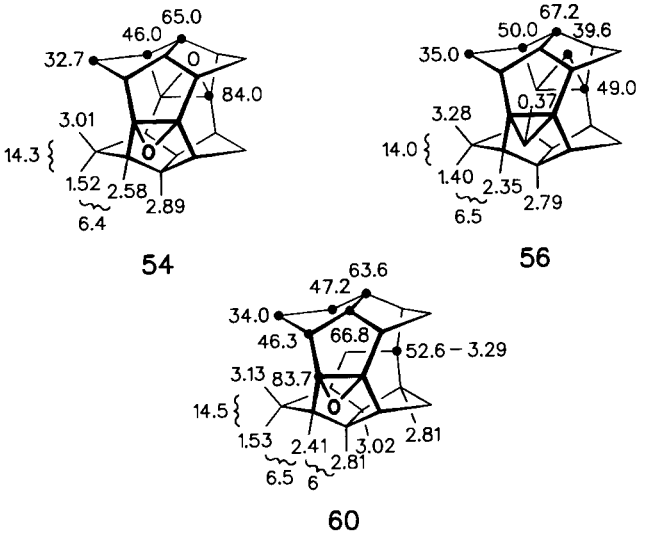


Figure 5. ^{1}H- and ^{13}C-NMR data [$CDCl_3$, δ, *J* (Hz)] for diepoxide **54**, bishomodiene **56**, and epoxide **60**

The X-ray structural data for **56** and **57**[4] (Figure 6) are in good agreement with the calculated relationship between molecular shape and hybridization of the central carbon atoms. For dioxide **57**, the transannular C,C distance (d_3) is shorter, the lateral C,C distance (d_2) larger than those for **56**. In this respect, **56** is expectedly closer to saturated **5** (**44**, Figure 4) than is **57** (**54**).

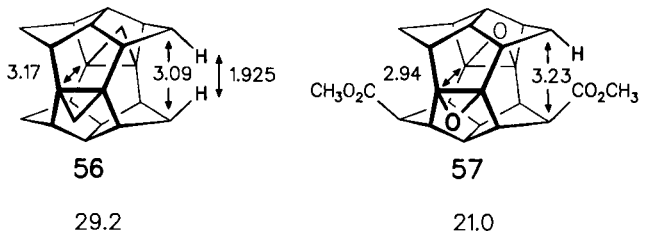
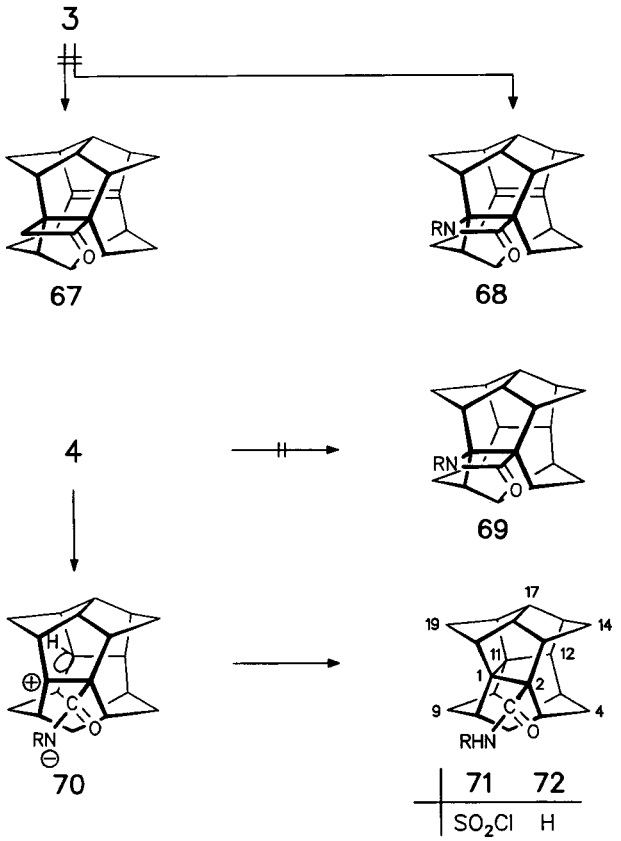


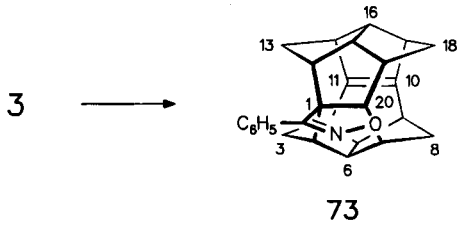
Figure 6. Selected experimental structural data (Å, X-ray) for bishomodiene **56** and diepoxy diester **57**

Annulation of a cyclobutanone (e.g. **67**) or a β-lactame ring (e.g. **68**) to **C** and **D** substrates potentially could be used for the installation of vicinal C,C and C,N substituents upon the molecular surface. Yet, after rather extensive efforts to add ketenes (from various sources) or isocyanates to diene **3** under various sets of conditions chosen to propagate "concerted"-type mechanisms[55], only bridged products of the secopagodane type **71** were observed besides polymers. The intervention of homoallylically stabilized ionic intermediates of type **H**[56] is highly probable as a consequence of severe steric constraints operative in concerted transition states. This explanation is further substantiated by the reaction of monoene **4** with chlorosulfonyl isocyanate[57] conducted at

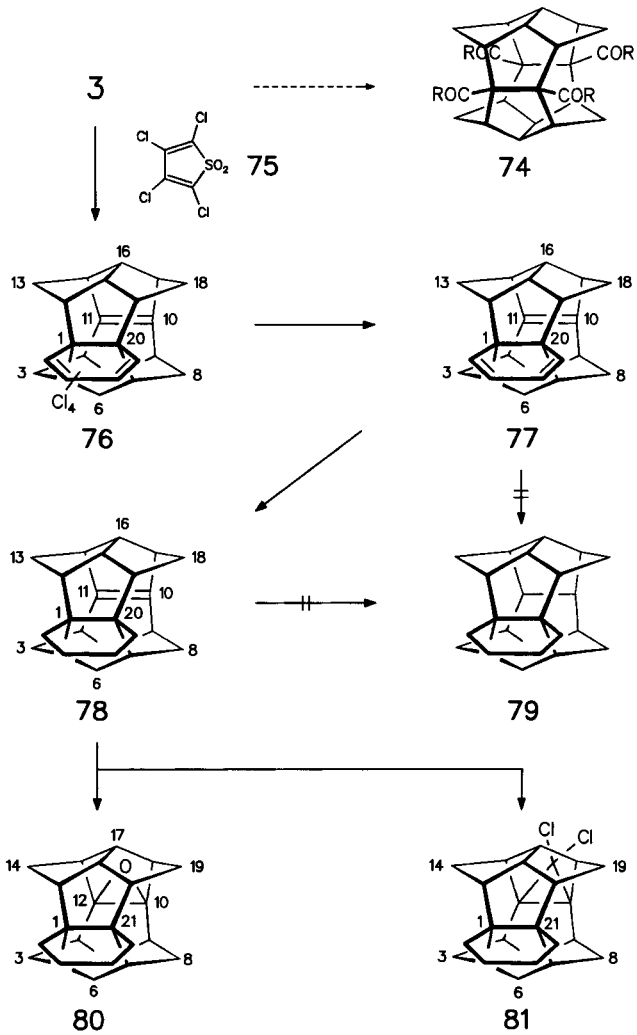
−30°C. After hydrolysis and reduction (Na_2SO_3) of the moisture-sensitive crude material (**71**), the major product was separated out of a rather complex mixture and identified (NMR, MS) as the secopagodanecarboxamide **72** (60 to 70%). Through-space "back-lobe stabilization"[58] as formulated in dipole **70** finds rather favorable geometrical assistance.



To achieve vicinal C,O functionalization, the diene **3** was probed for its reactivity towards nitrile oxides[59]. The respective transition states should profit from a relatively weak steric compression and the primary adduct **73** should have a live time sufficiently long to allow for a second addition. When chlorobenzaldoxime (5 equivalents to advance bisaddition) was added to the solution of **3** and triethylamine in deoxygenated CH_2Cl_2, total conversion was noted within minutes. According to TLC and ^{1}H-NMR control, one major product was accompanied by two components in trace amounts. They were identified after chromatography as C_s-symmetrical monoisoxazoline **73** (72%; m.p. >330°C), hydrate **24** and bisoxide **54**. After repetition of the experiment with **73** instead of **3**, again no bisisoxazoline was detected. Compound **73** survived heating to at least 330°C; in the mass spectrum [*m/z* (%) = 379 (6) [M^+], 260 (100)] facile dissociation into its [4 + 2] components was manifested. The ^{1}H- and ^{13}C-NMR analyses (C_s symmetry) were unequivocal except that the "left"/"right" assignment for the methylenic signals can be interchanged. The vicinal H,H coupling constants are typical for an olefinic ($J_{5,9}$ = 5 Hz) and a saturated side ($J_{2,6} = J_{5,6}$ = 10 Hz); the signals for the pyramidalized C-10(11) carbons (δ = 152.0, 151.8) appear in the expected absorption range (cf. Figure 4)[60].

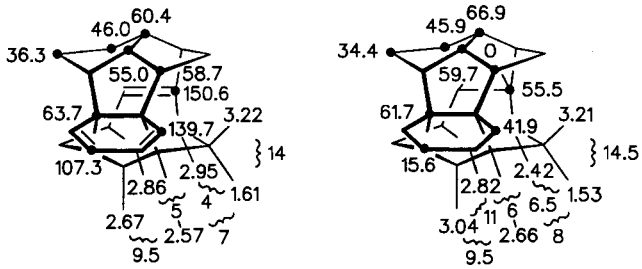


The quality of **3** as a dienophile was tested against the highly reactive tetrachlorothiophene dioxide (**75**)[64]. Twofold annulation by cyclohexadiene rings could ultimately be utilized for the introduction of two pairs of vicinal C,C substituents as e.g. in **74**. In line with a congested transition state, even in boiling xylene where **75** starts to decompose, addition proceeded rather slowly. From an optimized protocol with 15−20 equivalents of **75**, after ca. 90% conversion and SO_2 extrusion, the monoannulated C_s-symmetrical **76** was isolated in 58% yield with no indication (TLC, ^{1}H NMR) of the formation of a bisadduct. Compound **76** was dehalogenated according to standard methodology[65] to



triene **77** (95%, m/z = 312 (100%) [M^+]). Even under forcing conditions, hydrogenation of **77** over Pd/C ended with the formation of hyperstable cyclohexanobissecoene **78** (no **79**). Epoxidation and dichlorocarbene addition were again straight-forward (>90% **80** or **81**, respectively). It is mechanistically revealing that **78**, in contrast to **4**, resisted strong acids (CF_3CO_2H, HBr) for hours and could be exposed to ionic hydrogenation conditions ($CH_2Cl_2/CF_3CO_2H/Et_3SiH$; BF_3/Et_3SiH[66]) with no sign of **79** being detected.

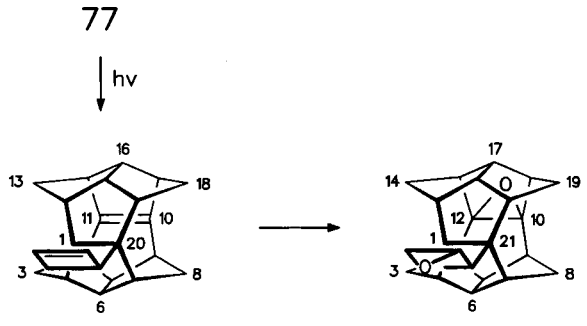
The completely assigned NMR spectra of **77** (Figure 7) with eight cleanly separated ^1H and nine ^{13}C signals exhibit the typical features of the "flat" unsaturated (cf. **26** in Figure 3) and the more spherical saturated sides. In the mass spectrum of **78** – cf. that of **73** – m/z = 260 resulting from elimination of the C_4H_8 chain is the most intense peak. For comparison with **77**, the ^1H- and ^{13}C-NMR data of **80** are included in Figure 7.



77 **80**

Figure 7. ^1H- and ^{13}C-NMR data [$CDCl_3$, δ, J (Hz)] of triene **77** and cyclohexano epoxide **80**

The cyclohexadiene part of **77** offered a detour for a four-membered ring annulation to **3**. Direct excitation with monochromatic 254-nm light (cyclohexane solution, low-pressure Hg lamp) induced uniform electrocyclization to **82** ($J_{2,3a}$ = 7; $J_{2,6}$ = 9; $J_{5,6}$ = 10 Hz), a behavior to be expected for such a rigidly clamped 1,3-cyclohexadiene[12,67] under the given excitation conditions. Mass and the (incompletely assigned) ^1H-/^{13}C-NMR spectra of **82** and of its quantitatively produced dioxide derivative **83** ($J_{2,3a}$ = 8; $J_{2,6}$ = 9, $J_{4,5}$ = 6, $J_{5,6}$ = 11 Hz) confirm the structures.



82 **83**

According to an X-ray analysis[4], the hyperstable **78** (Figure 8), a prototypical **D** structure, has a C=C bond length of 1.310 Å, and the olefinic carbons are pyramidalized by 9° (5.9° calculated for **4**). The transannular and lateral (d_3/d_2) distances are very similar to those in **56** (Figure 6) and clearly shorter than in the **E** structure **44** (Figure 4) while the lateral H/H distance (d_1) is even shorter by 0.11 Å. Significant line broadening of the C-2(7,14,19) signal (δ = 54.9) is suggestive of interconverting conformations for the annulated cyclohexane ring. The X-ray analysis indicates a boat conformation in the crystalline state.

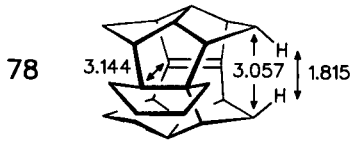


Figure 8. Selected transannular distances (X-ray) for cyclohexano ene **78**

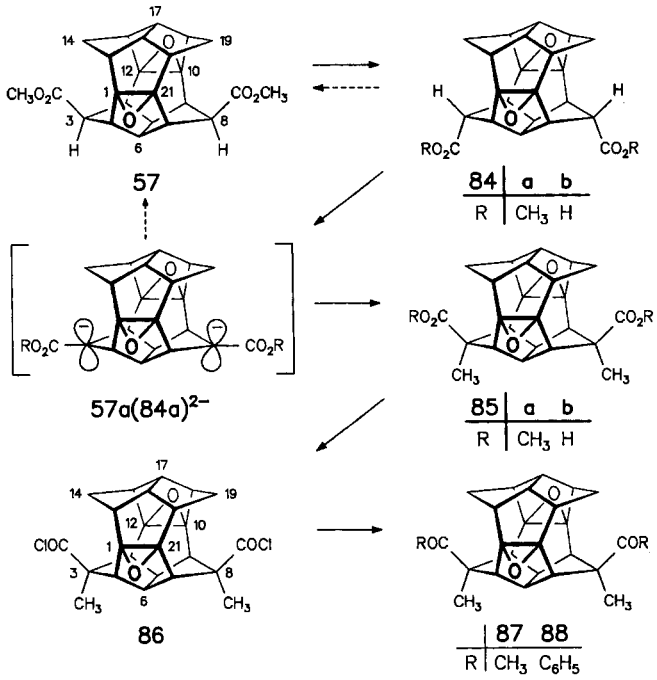
Reactivity Modulations in the Bissecododecahedrane Half-Cages

In the preceding paper[1], it was demonstrated for the secopagodane structure that there are significant reactivity differences at the two different lateral sides. For bissecododecahedranes, especially saturated ones with their even shorter lateral C/C (H/H) distances (Table 2), the manipulation of functionalities within and the installation of functionalities into these lateral half-cages should become even more problematic, if not impossible. The point being stressed with reference to selected examples, not detailed in the Experimental Section, is that the limited accessibility and limited space within these half-cages on the other hand can be put to preparative advantage.

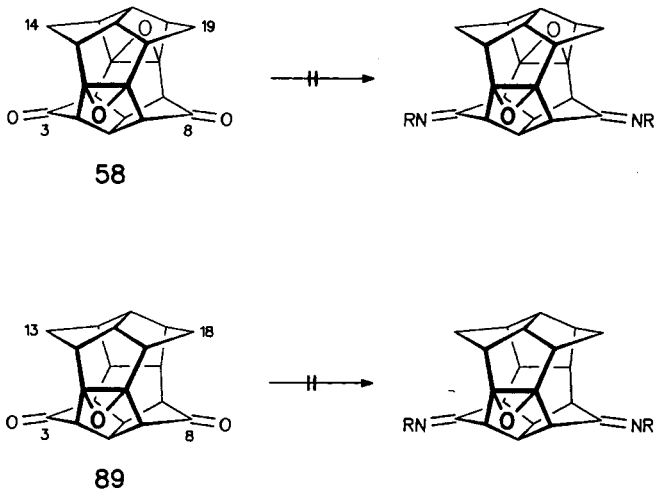
Saponification of the dimethyl *syn,syn*-pagodanedicarboxylate **6** with aqueous methanolic KOH solution led to mainly the *syn,syn*-diacid admixed with some of the *syn,anti*-isomer[1]. Saponification of the dimethyl diepoxy-*syn,syn*-dicarboxylate **57** with the same base system although needing more forcing conditions (130°C, 3 h) nevertheless produced quantitatively the stereochemically pure *anti,anti*-diacid **84b** ($\delta_{3,8\text{-H}}$ = 4.22) which was fully identified as dimethyl diester **84a**. Similarly, **57** was uniformly isomerized to **84a** with CH_3ONa/CH_3OH at 130°C (ampoule, 10 min). The *syn*-3(8)-hydrogens in **84a** are no longer accessible to this base and thus *syn*→*anti* epimerization presumably precedes the saponification.

Yet, with LDA/THF/CH_3I at −40°C, deprotonation and *anti*-specific methylation to give a quantitative yield of **85a**, not necessarily via the dianion depicted, were brought about. Alkaline saponification of **85a** was even slower: refluxing in ethylene glycol for 6 h (200°C) was needed for its total conversion into diacid **85b**. Not unexpectedly, the transformation of diacid **85b** into bis(acid chloride) **86** by oxalyl chloride is sufficiently rapid in boiling benzene with DMF catalysis. Bis(acid chloride) **86** remarkably survived treatment with an excess of MeLi at −20°C, an aqueous workup at room temperature and filtration over silica gel. It is only after raising the reaction temperature to ca. 25°C

that **86** added MeLi to provide the bis(methyl ketone) **87**, but it still remained unaffected by C_6H_5Li and C_6H_5MgCl under similar conditions. With diphenylcadmium[68], though, bis(phenyl ketone) **88** was produced.



As carbene sources – and thus as substrates for the installation of the lateral bonds on the way to pentagonal and homodecahedranes – bishydrazones of bissecodiones **58** or **89** were of interest. Unfortunately, in no case could a condensation with hydrazine or tosylhydrazine be achieved, in line with earlier observations for secopagodane structures[1].



As an exemplary display of the steric consequences resulting from nucleophile additions to functionalities embedded into bissecododecahedrane half-cages, a dihydrate of diepoxy diketone **58** (**90**) has been simulated as a model for the required intermediates (Figure 9)[69]. With shortest distances of 2.28–2.34 Å between *syn*-methylene hydrogens and opposite oxygen atoms far smaller than the van der Waals limit, the resistance against such a (transition state) situation is very apparent.

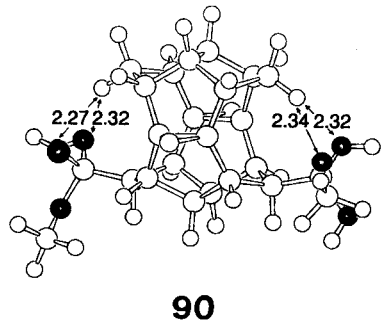


Figure 9. Calculated (MM2) structure of hypothetical dihydrate **90**

Summary: The bissecododecahedradienes **C**, which are readily prepared from pagodanes as intermediates on the way to dodecahedranes, make up a fascinating class of bent, strictly *syn*-periplanar, bridgehead dienes in their own right. Unusually strong transannular interactions in their sterically well protected, rigid molecular interior give rise to unusual if not unique physical and chemical phenomena. Although from calculation comparably hyperstable, the minimization of the strong π/π destabilization in these dienes renders the hydrogenation of one of the two C,C double bonds (**C** → **D**) possible. Yet, the strict resistance of the derived bissecomonoenes **D** towards hydrogenative saturation thwarts the realization of route B for the stepwise pagodane → dodecahedrane transformation along the conceptually most direct pathway. Somewhat disappointingly, reduction of the steric H/H interactions on the molecular surfaces by the installation of two ketonic functions (**13**, **14**) proved not to be a sufficient measure to overcome this barrier[70]. The bissecomonoenes **D** are also found to be absolutely reluctant in [4 + 2] cycloaddition reactions; saturation can, however, be achieved by epoxidation, carbene addition, and hydroxylation. Consequently, in the bissecodienes **C** both double bonds can be saturated by these latter methodologies in a manner affording high yields of products. Of help for the execution of these saturation reactions, for the understanding of their procedere, and for the characterization of the respective products there have been a host of analogies as well as discrepancies concerning the wealth of literature reports on structurally related dienes and monoenes[3,23] – specifically on the similarly *syn*-periplanar, yet even more proximate tricyclo[4.2.2.2^{2,5}]dodeca-1(2),5(8)-diene[71], on torsionally distorted *meso*-bridgehead dienes[72], on bicyclo[3.3.0]oct-1(5)-enes[73], and on sesquinorbornenes[74]. A limitation for further functionalization of the unsaturated bissecododecahedrane skeletons in ways which potentially are more suitable for subsequent preparative goals is caused by the high propensity for transannular bonding via cationic and radicaloid intermediates. Nevertheless, a large number of variously functionalized saturated bissecododecahedranes is ready to be probed for the instal-

lation of the two lateral bonds which are still missing for the development into to pentagonal dodecahedranes[26].

Support by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *BASF AG* is gratefully acknowledged. B. A. R. C. M. and P. R. S. thank the *Alexander-von-Humboldt-Stiftung* for fellowships. We thank Dr. *J. Wörth* for assistance with the mass spectra, Dipl.-Chem. *F. Wahl* for supplementary force-field calculations, and Dr. *L. Knothe* for his help with the preparation of the manuscript.

Experimental

Melting points: Bock Monoscop M. – Analytical TLC: Merck silica gel plates with F_{254} indicator. – Flash chromatography: 0.04–0.06 mm silica gel, Macherey & Nagel. – Analytical GC: Varian 3700, glass capillary column 25 m, OV17, FID; integrator Varian CDS 111. – IR: Perkin-Elmer 457, Philips PU 9706. – Raman: Jobin Yvon U 1000. – UV: Perkin-Elmer Lambda 15. – ^{1}H NMR: Bruker WM 250, WM 400; if not specified differently, the 250-MHz spectra are given; ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts relative to TMS (δ = 0), coupling constants in Hz; for signal assignment standard techniques such as homo and heteronuclear decoupling experiments or 2D FT COSY or heteroccorrelation spectra were employed; assignments indicated with * can be interchanged; generally, the H,H and C,H connectivities were established by two-dimensional homo- and heteronuclear-correlated spectra. Whenever necessary, NOE measurements were performed to elucidate stereochemical (transannular) relationships. – MS: Finnigan MAT 44S.

Photolyses of Dienes **3** (**8**, **13**): Ca. 10^{-3} M degassed solutions of dienes **3** (**8**, **13**) in ether (quartz vessel, high-pressure mercury lamp, room temp.) or in acetone (pyrex vessel, 250-W medium pressure mercury lamp, room temp.) are irradiated; ^{1}H-NMR monitoring and product analysis (GC) confirm quantitative conversion into the respective pagodanes **1** (**6**, **11**)[1].

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-1(20)-ene (**4**): To a solution of diene **3** (100 mg, 0.38 mmol) in a degassed mixture of EtOH (15 ml) and THF (30 ml), stirred in an inert atmosphere at 0°C, is added a hydrazine hydrate solution (20 ml, 99%) in one portion, then slowly a H_2O_2 solution (20 ml, 30%) (**Caution**, very exothermic, intensive external cooling is necessary!) The mixture is stirred at 0°C for 4 h and at room temp. for 12 h, then diluted with CH_2Cl_2 (200 ml) and extracted with H_2O (for a better separation of the phases, conc. NaCl solution may be added). The organic phase is dried ($MgSO_4$) and concentrated in vacuo to give **4** (96 mg, 95%) as colorless crystals, m.p. 332–333°C (isomerization to **17**). – IR (KBr): $\tilde{\nu}$ = 3010, 2920, 2880, 2840 (C–H) cm^{-1}. – Raman (powder): 1625 (C=C) cm^{-1}. – ^{1}H and ^{13}C NMR (C_6D_6): Figure 1. – MS (EI): *m/z* (%) = 262 (100) [M$^+$].

Dimethyl Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-1(20)-ene-syn-3,syn-8-dicarboxylate (**9**): To a solution of **8**[1] (50 mg, 0.13 mmol) in a mixture of MeOH (2 ml) and ethyl acetate (2 ml) is added hydrazine hydrate (1 ml, 80%) and then with stirring HgO (1 g) in portions over 1 h. The mixture is diluted with CH_2Cl_2, extracted with 1% HCl solution, and filtered through silica gel to give **9** (48 mg, 95%) as colorless crystals, m.p. 225–227°C. – IR (KBr): $\tilde{\nu}$ = 2980, 2940 (C–H), 1725 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.75 (s, 2 OCH_3), 3.39 (m, 10-, 11-H), 3.26 (m, 2-, 7-H), 2.77–2.98 (m, 9 H), 2.60 (m, 1 H), 2.55 (m, 3*a*-, 8*a*-H), 2.04 (d, 13*s*-, 18*s*-H), 1.59 (m, 13*a*-, 18*a*-H); $J_{13a,\,13s}$ = 14.4. – MS (EI): *m/z* (%) = 378 (30) [M$^+$], 347 (100).

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0,^{12,16}.0^{15,19}]icos-1(20)-ene-3,8-dione (**14**): To a solution of crude diene **13**[1] (101 mg, 0.35 mmol) and hydrazine hydrate (35 mg, 0.7 mmol) in CH_2Cl_2/MeOH (2:3, 5 ml) is added with stirring yellow HgO (150 mg, 0.7 mmol) at room temp. over a period of 15 min. The mixture is stirred for a further 15 min, then filtered and the filtrate concentrated in vacuo to give a colorless solid. Filtration over a short column of silica gel (10% ethyl acetate/CH_2Cl_2) affords **14** (90 mg, 89%), m.p. >340°C (rearr.). – ^{1}H NMR (400 Hz, $CDCl_3$): Figure 1. – ^{13}C NMR ($CDCl_3$): Figure 1.

Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**18**): On heating to 330°C for 15 min, a sample of **14** rearranges cleanly to **18**. – ^{1}H NMR ($CDCl_3$): δ = 3.19 (m, 6-, 7-H), 2.88 (m, 16-, 17-H), 2.78 (t, 2-, 12-H), 2.58 (m, 3-, 5-H), 2.44 (m, 13-, 15-H), 2.22 (d, 14*s*-H), 2.18 (m, 18-, 20-H), 2.03 (m, 8-, 10-H), 1.85 (m, 19*a*-H), 1.53 (dt, 14*a*-H), 1.52 (m, 19*s*-H); $J_{2,3}$ = $J_{2,15}$ = 9.7, $J_{14s,14a}$ = 14.7, $J_{19s,19a}$ = 11.2.

Addition of Bromine to Dienes **3** (**13**) → **19** (**21**): To solutions of **3** (**13**) [130 (145) mg] in dry CCl_4 (5 ml) is added bromine (125 mg). After total conversion (30 min, TLC) and concentration in vacuo, pure dibromides **19** (**21**)[1] are isolated.

2-Chlorodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**22**): Through a solution of **3** (50 mg, 0.19 mmol) in dry CH_2Cl_2 (5 ml) is passed a stream of HCl (dried over P_2O_5 and conc. H_2SO_4). Total conversion after 3 min (TLC). Concentration in vacuo gives practically pure **22** as a colorless solid. Purification is generally accompanied by partial hydrolysis (i.a. **24** can be detected by ^{1}H-NMR spectrometry). – IR (KBr): $\tilde{\nu}$ = 3000, 2924, 2852 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.97 (t, 3-, 15-H), 2.79 (d, 4*s*-, 14*s*-H, m, 7-, 16-H), 2.66 (m, 6-, 17-H), 2.59 (8-, 20-H), 2.44 (m, 12-H), 2.29 (m, 5-, 13-H), 1.98 (m, 9*s*-, 19*s*-H), 1.96 (m, 10-, 18-H), 1.43 (m, 9*a*-, 19*a*-H), 1.37 (m, 4*a*-, 14*a*-H); $J_{3,4a}$ = 6, $J_{3,7}$ = 6, $J_{4a,4s}$ = 13.5, $J_{4a,5}$ = 6, $J_{5,12}$ = 9, $J_{6,7}$ = 10.5, $J_{7,8}$ = 4, $J_{9a,9s}$ = 11.0. – ^{13}C NMR ($CDCl_3$): δ = 104.6 (C-2), 76.8 (C-1), 70.3 (C-11), 59.7 (C-6, -17), 58.7 (C-7, -16), 54.4 (C-12), 53.3 (C-3, -15), 45.3 (C-10, -18), 44.1 (C-8, -20), 39.3 (C-5, -13), 36.3 (C-9, -19), 34.8 (C-4, -14). – MS (EI): *m/z* (%) = 296 (6) [M$^+$], 262 (30), 261 (100).

Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosan-2-ol (**24**): Colorless crystals, m.p. >330°C, brownish discoloration above 280°C. – IR (KBr): $\tilde{\nu}$ = 3013, 2936, 2865, 2692 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.75 (d, 4*s*-, 14*s*-H), 2.72 (m, 7-, 16-H), 2.66 (m, 6-, 17-H), 2.46 (m, 12-H), 2.30 (m, 8-, 20-H)*, 2.27 (m, 5-, 13-H)*, 2.22 (m, 3-, 15-H), 1.91 (m, 9*s*, 19*s*-, 10-, 18-H), 1.56 (s, OH), 1.45 (m, 9*a*-, 19*a*-H), 1.37 (m, 4*a*-, 14*a*-H); $J_{3,4a}$ = $J_{4a,5}$ = $J_{3,7}$ = 6, $J_{4a,4s}$ = 13.5, $J_{5,12}$ = 9, $J_{6,7}$ = 12, $J_{9a,9s}$ = 9. – ^{13}C NMR ($CDCl_3$): δ = 96.4 (C-2), 73.9 (C-1), 68.5 (C-11), 59.8 (C-6, -17), 58.5 (C-7, -16), 54.7 (C-12), 50.3 (C-3, -15), 44.7 (C-10, -18), 41.6 (C-5, -13), 39.4 (C-8, -20), 36.6 (C-9, -19), 33.8 (C-4, -14). – MS (EI): *m/z* (%) = 278 (12) [M$^+$], 261 (22), 260 (100).

2-(3-Chlorobenzoyloxy)decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**25**): Colorless crystals, m.p. 243–245°C. – IR (KBr): $\tilde{\nu}$ = 3500 (OH), 3034, 3012, 2956, 2863 (C–H), 1693 (C=O) cm^{-1}. – ^{1}H NMR: ($CDCl_3$): δ = 7.98 (m, 2′-H), 7.92 (m, 6′-H), 7.52 (m, 4′-H), 7.39 (t, 5′-H), 3.01 (d, 4*s*-, 14*s*-H), 2.78 (m, 3-, 6-, 15-, 17-H), 2.73 (m, 7-, 16-H), 2.65 (m, 8-, 20-H), 2.49 (m, 10-, 18-H), 2.33 (t, 5-, 13-H), 2.03 (br. d, 9*s*-, 19*s*-H), 1.60 (m, 9*a*-, 19*a*-H), 1.55 (s, OH), 1.49 (m, 4*a*-, 14*a*-H); $J_{3,4a}$ = $J_{5,4a}$ = 6, $J_{4a,4s}$ = 13.5, $J_{6,7}$ = $J_{9a,9s}$ = 10. – ^{13}C NMR ($CDCl_3$): δ = 164.3 (C=O), 134.5 (C-1′), 134.0 (C-3′), 132.6 (C-2′), 129.6 (C-6′), 129.3 (C-4′), 127.5 (C-5′), 108.3 (C-2), 95.8 (C-12), 75.7 (C-11), 74.3 (C-1), 58.3 (C-6, -17), 58.2 (C-7, -16), 50.2 (C-5, -13), 46.9 (C-3, -15), 42.6 (C-8, -20), 41.8

(C-10, -18), 36.1 (C-9, -19), 32.7 (C-4, -14). – MS (CI, methane): *m/z* (%) = 433 (12%) [M^+], 417 (20), 415 (56), 278 (22), 277 (100).

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-10-ene-1,20-diol (**26**): To a solution of **3** (200 mg, 0.77 mmol) in dry benzene (20 ml) at room temp. in an inert atmosphere is added a solution of OsO_4 (235 mg, 0.92 mmol) in dry benzene (10 ml) with stirring in one portion (in a closed flask because of the vapor pressure of OsO_4!). After a few minutes, a microcrystalline, greenish precipitate begins to settle (identified as osmate monoester **33** by ^{1}H NMR). After total conversion (12–24 h, TLC control), the reaction mixture is concentrated and suspended in dry THF (100 ml). In an inert atmosphere, $LiAlH_4$ is added in small portions, till the green color has disappeared completely. Excess of $LiAlH_4$ is cautiously destroyed with wet THF, then the mixture is diluted with H_2O (200 ml) and extracted with CH_2Cl_2. The organic phase is dried ($MgSO_4$), filtered over a short pad of silica gel, and the filtrate concentrated in vacuo to give **26** (192 mg, 85%), colorless crystals (CH_2Cl_2/ether), no m.p. up to 330°C, brownish discoloration above 240°C. – IR (KBr): $\tilde{\nu}$ = 3326 (OH), 3016, 2924, 2884 (C–H) cm^{-1}. – ^{1}H and ^{13}C NMR ($CDCl_3$): Figure 3. – MS (EI): *m/z* (%) = 294 (20) [M^+], 276 (100), 181 (68), 167 (52), 155 (78), 128 (80), 115 (100).

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane-1,20-diol (**27**): To a solution of **4** (100 mg, 0.38 mmol) in dry benzene (50 ml) is added at room temp. with stirring a solution of OsO_4 (116 mg, 0.46 mmol) in benzene (10 ml). After 1 h, the solution becomes opaque, and a brownish-green precipitate begins to settle (osmate mono ester **45**, ^{1}H NMR). After total conversion (36–48 h, TLC control), the mixture is concentrated in vacuo, the residue dissolved in dry THF (50 ml), and $LiAlH_4$ is added in small portions in an inert atmosphere till the brownish-green color has disappeared completely. Excess of $LiAlH_4$ is cautiously destroyed with wet THF, then H_2O (200 ml) is added and the mixture extracted exhaustively with CH_2Cl_2. The organic phase is repeatedly washed with H_2O, dried ($MgSO_4$), and filtered over a short pad of silica gel. Concentration in vacuo gives **27** (108 mg, 96%) as a colorless powder, m.p. >330°C, which is crystallized from ethyl acetate/CH_2Cl_2 (1:1). – IR (KBr): $\tilde{\nu}$ = 3320 (OH), 3034, 2920, 2846 (C–H) cm^{-1}. – ^{1}H and ^{13}C NMR ($CDCl_3$): Figure 3. – MS (EI): *m/z* (%) 296 (100), 91 (100).

$C_{20}H_{24}O_2$ (296.4) Calcd. C 81.04 H 8.16
Found C 81.14 H 8.23

Octacyclo[8.8.1.1^{8,14}.0^{2,6}.0^{3,17}.0^{4,15}.0^{9,13}.0^{12,16}]icos-15-ene-7,19-dione (**29**): To a solution of **3** (100 mg, 0.38 mmol) in acetone/H_2O/CH_2Cl_2 (1:1:1, 20 ml) are added at –35°C KOH (50 mg) and $KMnO_4$ (600 mg, 3.8 mmol). The mixture is warmed to 0°C over a period of 2 h. (TLC control, total conversion, one main product). The reaction mixture is diluted with aqueous $Na_2S_2O_5$ solution (200 ml) and extracted with CH_2Cl_2. The organic phase is dried ($MgSO_4$), filtered over a short pad of silica gel, and the filtrate concentrated in vacuo to give colorless crystals (108 mg, 96%), no m.p. up to 350°C, above 250°C brownish discoloration. – IR (KBr): $\tilde{\nu}$ = 2980, 2920, 2900, 2875 (C–H), 1658 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): Figure 3. – ^{13}C NMR ($CDCl_3$/C_6D_6, 1:1): Figure 3. – MS (CI, CH_4): *m/z* (%) = 293 (100) [M^+ + 1], 277 (12), 264 (M^+ – CO, 12); MS (EI): 292 (10) [M^+], 264 (100) [M^+ – CO], 193 (60), 181 (100), 167 (58), 165 (55), 155 (100).

1,20-(Carbonyldioxy)nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-10-ene (**35**): To a solution of **26** (50 mg, 0.17 mmol) in dry CH_2Cl_2 (20 ml) in an inert atmosphere is added iminophosphorane base BEMP [(2-*tert*-butylimino)-2-(diethylamino)-1,3-dimethyl-1,3,2-diazaphosphinane[40]] (233 mg, 0.85 mmol), and the mixture is stirred at room temp. for 5 min. Trichloroacetyl chloride (34 mg, 0.19 mmol) is added and the mixture stirred to total conversion (ca. 30 min, TLC control). After dilution with H_2O (100 ml), the product is extracted exhaustively into CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), and filtered over a short pad of silica gel. Concentration of the filtrate in vacuo gives **35** (50 mg, 92%), colorless oxygen- and acid-sensitive crystals (CH_2Cl_2/ether), no m.p., above 170°C brownish discoloration and decomposition. – IR (KBr): $\tilde{\nu}$ = 3014, 2926 (C–H), 1772 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.21 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.10 (m, 6-, 15-H), 2.98 (m, 4-, 9-, 12-, 17-H), 2.90 (m, 2-, 7-, 14-, 19-H), 2.86 (m, 5-, 16-H), 1.71 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7, $J_{3a,3s}$ = 14, $J_{3a,4}$ = 4, $J_{4,5}$ = 4.5, $J_{5,6}$ = 10, $J_{6,7}$ = 9. – ^{13}C NMR ($CDCl_3$): δ = 152.1 (C-10, -11), 112.5 (C-1, -20), 59.9 (C-5, -16), 59.3 (C-6, -15), 54.3 (C-2, -7, -14, -19), 45.6 (C-4, -9, -12, -17), 36.5 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 320 (100) [M^+], 276 (65) [M^+ – CO_2], 245 (40), 147 (45).

1,20-Dimethoxynonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-10-ene (**36**): A solution of **26** (100 mg, 0.34 mmol) in dry THF (50 ml) is stirred at room temp. in an inert atmosphere with NaH (41 mg, 1.7 mmol) and methyl iodide (241 mg, 1.7 mmol) to total conversion (6-12 h, TLC control). Excess of NaH is cautiously destroyed with wet THF, the mixture then diluted with H_2O (200 ml) and extracted with CH_2Cl_2. The organic phase is dried ($MgSO_4$), concentrated in vacuo, the yellowish residue dissolved in CH_2Cl_2 and the solution filtrated through a short pad of silica gel. Concentration in vacuo gives colorless, oxygen- and acid-sensitive crystals (105 mg, 96%), m.p. 162–164°C. – IR (KBr): $\tilde{\nu}$ = 3046, 3016, 2958, 2932, 2874, 2842, 2814 (C–H) cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 3.35 (s, 2 OCH_3), 3.09 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 2.99 (m, 6-, 15-H), 2.91 (m, 4-, 9-, 12-, 17-H), 2.89 (m, 2-, 7-, 14-, 19-H), 2.77 (m, 5-, 16-H), 1.72 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7, $J_{3a,3s}$ = 13.5, $J_{3a,4}$ = 4.5, $J_{4,5}$ = 4, $J_{5,6}$ = $J_{6,7}$ = 10. – ^{13}C NMR ($CDCl_3$): δ = 150.6 (C-10, -11), 106.9 (C-1, -20), 60.2 (C-5, -16), 58.5 (C-6, -15), 52.1 (C-2, -7, -14,-19), 51.1 (2 OCH_3), 45.8 (C-4, -9, -12, -17), 37.6 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 322 (32) [M^+], 307 (20), 291 (100) [M^+ – OCH_3], 277 (92), 260 (60) [M^+ – 2 OCH_3].

$C_{22}H_{26}O_2$ (322.5) Calcd. C 81.95 H 8.13
Found C 81.83 H 8.19

1,20-Bis(benzyloxy)nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-10-ene (**37**): A solution of **26** (100 mg, 0.34 mmol) in dry THF (20 ml) is stirred at room temp. in an inert atmosphere with NaH (41 mg, 1.7 mmol) and benzyl bromide (291 mg, 1.7 mmol) to total conversion (ca. 24 h, TLC control). Excess of NaH is destroyed cautiously with wet THF, the reaction mixture then diluted with H_2O (200 ml) and extracted with CH_2Cl_2. Remaining benzyl bromide is removed by column chromatography (cyclohexane/ethyl acetate, 1:1). Concentration of the eluate in vacuo gives colorless, oxygen- and acid-sensitive crystals (150 mg, 93%), m.p. 103–105°C, sufficiently pure (^{1}H NMR) for further utilization. – IR (KBr): $\tilde{\nu}$ = 3004, 2938, 2878 (C–H) cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 7.40 (m, 23-H), 7.28 (m, 24 h), 7.20 (m, 25-H), 4.69 (s, 21-H), 3.21 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.04 (m, 2-, 6-, 7-, 14-, 15-, 19-H), 2.95 (m, 4-, 9-, 12-, 17-H), 2.82 (m, 5-, 16-H), 1.73 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{3a,3s}$ = 14. – ^{13}C-NMR ($CDCl_3$): δ = 150.7 (C-10, -11), 140.9 (C-22), 128.0 (C-24), 126.7 (C-23), 126.5 (C-25), 107.4 (C-1, -20), 65.5 (C-21), 60.4 (C-5, -16), 58.5 (C-6, -15), 53.0 (C-2, -7, -14, -19), 45.8 (C-4, -9, -12, -17), 37.5 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 383 (10) [M^+ – $CH_2C_6H_5$], 367 (14), 293 (15), 278 (60), 277 (98), 91 (100).

21-Oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane-10,11-diol (**38a**): To a stirred solution of **26** (100 mg, 0.34

mmol) in CH_2Cl_2 (50 ml) at room temp. is added benzoylperoxycarbamic acid[39] (74 mg, 0.41 mmol), and the mixture is stirred to total conversion (ca. 6 h, TLC control). After filtration over a short pad of silica gel and concentration in vacuo, benzamide is removed by sublimation in vacuo (10^{-2} Torr/60°C). Colorless crystals (103 mg, 98%), m.p. >350°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 3556, 3472 (OH), 3026, 2924, 2856 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.39 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.15 (m, 5-, 16-H), 2.83 (m, 4-, 9-, 12-, 17-H), 2.81 (m, 6-, 15-H), 2.67 (s, OH), 2.47 (t, 2-, 7-, 14-, 19-H), 1.64 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a} = J_{2,6} = 6$, $J_{3a,3s} = 15$, $J_{3a,4} = 8$, $J_{4,5} = J_{5,6} = 10.5$. – ^{13}C NMR ($CDCl_3$): δ = 98.1 (C-10, -11), 83.3 (C-1, -20), 65.8 (C-6, -15), 58.1 (C-4, -9, -12, -17), 56.7 (C-5, -16), 45.7 (C-2, -7, -14, -19), 33.9 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 311 (28) [M^+ + 1], 310 (100) [M^+].

10,11-Dimethoxy-21-oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane (**38b**): A solution of **36** (50 mg, 0.15 mmol) in CH_2Cl_2 (5 ml) is stirred at room temp. with benzoylperoxycarbamic acid (33 mg, 0.18 mmol) to total conversion (TLC control, ca. 4 h). The mixture is concentrated in vacuo, the residue dissolved in CH_2Cl_2, the solution filtrated over a short pad of silica gel, and remaining benzamide removed by sublimation in vacuo (10^{-2} Torr/60°C) to give **38b** (50 mg, 97%), colorless crystals, m.p. 138–140°C (ether). – IR (KBr): $\tilde{\nu}$ = 3028, 2934, 2848, 2812 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.44 (s, OCH_3), 3.27 (m, 5-, 16-H), 3.24 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.12 (m, 4-, 9-, 12-, 17-H), 2.82 (m, 6-, 15-H), 2.49 (t, 2-, 7-, 14-, 19-H), 1.73 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a} = J_{2,6} = 6$, $J_{3a,3s} = 14.5$, $J_{3a,4} = 7$, $J_{4,5} = 10.5$, $J_{5,6} = 11.5$. – ^{13}C NMR ($CDCl_3$): δ = 105.5 (C-10, -11), 83.4 (C-1, -20), 65.7 (C-6, -15), 58.3 (C-5, -16), 52.7 (C-4, -9, -12, -17), 51.0 (OCH_3), 46.0 (C-2, -7, -14, -19), 35.0 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 338 (48) [M^+], 323 (30), 276 (96) [M^+ – 2 OCH_3].

10,11-Bis(benzyloxy)-21-oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane (**38c**): A solution of **37** (50 mg, 0.1 *mmol) in* CH_2Cl_2 (10 ml) is stirred at room temp. with benzoylperoxycarbamic acid (22 mg, 0.12 mmol) to total conversion (24 h, TLC control). After concentration in vacuo, the benzamide is removed by sublimation in vacuo (10^{-2} Torr/60°C) to give **38c** (48.5 mg, 94%), colorless crystals, m.p. 175–177°C (ether). – IR (KBr): $\tilde{\nu}$ = 3080, 3054, 3024, 2934, 2854 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.39 (m, 23-H), 7.28 (m, 24-H), 7.21 (m, 25-H), 4.72 (s, 21-H), 3.32–3.17 (m, 4-, 5-, 9-, 12-, 16-, 17-H), 3.29 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 2.83 (m, 6-, 15-H), 2.49 (t, 2-, 7-, 14-, 19-H), 1.70 (3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a} = J_{2,6} = 6.5$, $J_{3a,3s} = 14.5$, $J_{3a,4} = 7.5$, $J_{5,6} = 9$. – ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-22), 128.2 (C-24), 126.8 (C-23, -25), 106.0 (C-10, -11), 83.5 (C-1, -20), 66.0 (C-6, -15), 65.7 (C-21), 58.2 (C-5, -16), 53.8 (C-4, -9, -12, -17), 46.0 (C-2, -7, -14, -19), 34.9 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 399 (5) [M^+ – $CH_2C_6H_5$], 307 (5) (M^+ – 2 $CH_2C_6H_5$], 276 (30), 91 (100).

5-Oxanonacyclo[9.8.1.1^{17,18}.0^{3,18}.0^{4,6}.0^{4,9}.0^{6,17}.0^{8,12}.0^{15,19}]henicosane-14,20-dione (**39**): A solution of **29** (50 mg, 0.17 mmol) in CH_2Cl_2 (20 ml) is stirred with benzoylperoxycarbamic acid (37 mg, 0.20 mmol) at room temp. for 2 h (total conversion, TLC control). Filtration over a short pad of silica gel, concentration in vacuo, and removal of benzamide by sublimation in vacuo (10^{-2} Torr/ca. 60°C) gives **39** (50 mg, 96%) as a colorless powder which is crystallized from ethyl acetate, m.p. >350°C. – IR (KBr): $\tilde{\nu}$ = 3006, 2926, 2871 (C–H), 1663 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.50 (m, 1-, 11-, 13-, 15-H), 3.38 (m, 12-, 19-H), 3.03 (d, 2*s*-, 10*s*-, 16*s*-, 21*s*-H), 2.97 (m, 8-, 18-H), 2.66 (t, 3-, 7-, 9-, 17-H), 1.86 (m, 2*a*-, 10*a*-, 16*a*-, 21*a*-H); $J_{1,2a} = 9$, $J_{1,19} = 11.5$, $J_{2a,2s} = 15$, $J_{2a,3} = J_{3,18} = 5.5$, $J_{8,12} = 11$. – ^{13}C NMR ($CDCl_3$): δ = 212.4 (C-14, -20), 82.6 (C-4, -6), 67.6 (C-8, -18), 55.5 (C-1, -11, -13, -15), 51.3 (C-12, -19), 46.0 (C-3, -7, -9, -17), 34.5 (C-2, -10, -16, -21). – MS (CI): *m/z* (%) = 309 (100) [M^+ + 1]; (EI): 280 (40) [M^+ – CO], 215 (30), 169 (32), 115 (38), 91 (64), 79 (55), 77 (72), 65 (62), 55 (100).

10,11-Dimethoxynonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane-1,20-diol (**41**): To a solution of **36** (100 mg, 0.31 mmol) in dry benzene (20 ml), OsO_4 (95 mg, 0.37 mmol) in benzene (7 ml) is added at room temp. The solution soon becomes opaque and a brownish-green precipitate settles (osmate monoester). The mixture is stirred to total conversion (TLC control), then the solvent is removed and the brownish-green residue suspended in dry THF. With vigorous stirring in an inert atmosphere $LiAlH_4$ is added till the brownish-green color had disappeared (for the cleavage of the osmate monoester possibly slight warming is necessary). Excess of $LiAlH_4$ is cautiously destroyed with wet THF and the mixture diluted with H_2O (200 ml) and extracted exhaustively with CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo. The slightly yellowish residue is purified by chromatography (ethyl acetate/CH_2Cl_2). First **26** (5 mg, 4%) is eluted, then **41** (102 mg, 92%), colorless crystals, m.p. >330°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 3436 (OH), 2918 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.51 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.35 (s, OCH_3), 3.15 (m, 6-, 15-H), 3.06 (m, 5-, 16-H), 2.96 (m, 2-, 7-, 14-, 19-H), 2.93 (s, 2 OH), 2.70 (m, 4-, 9-, 12-, 17-H), 1.77 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a} = 7.5$, $J_{2,6} = 10$, $J_{3a,3s} = 15$, $J_{4,5} = 10$, $J_{5,6} = 1$. – ^{13}C NMR ($CDCl_3$): δ = 104.2 (C-1, -20), 97.0 (C-10, -11), 59.4 (C-6, -15), 58.2 (C-4, -9, -12, -17), 57.8 (C-5, -16), 52.4 (C-2, -7, -14, -19), 50.9 (4 OCH_3), 35.9 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 356 (31) [M^+], 341 (60) [M^+ – CH_3], 294 (62), 276 (100).

10,11-Bis(benzyloxy)nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane-1,20-diol (**42**): To a solution of **37** (200 mg, 0.42 mmol) in dry benzene (50 ml) OsO_4 (128 mg, 0.50 mmol) in benzene (10 ml) is added at room temp. After ca. 1 d, the yellow solution becomes opaque and a brownish-green precipitate settles (osmate mono-ester). The mixture is stirred to total conversion (2–3 d, TLC control), then concentrated and the brownish green residue suspended in dry THF. $LiAlH_4$ is added in small portions till the brownish-green color has disappeared completely. Excess of $LiAlH_4$ is destroyed cautiously by wet THF, the mixture diluted with H_2O (200 ml) and then extracted exhaustively with CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo. The yellowish residue is purified by chromatorgraphy (ethyl acetate/cyclohexane) to give **42** (188 mg, 88%), colorless crystals, m.p. 210–212°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 3426, 3372 (OH), 3050, 3026, 2926, 2842 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.36 (m, 23-H), 7.28 (m, 24-H), 7.22 (m, 25-H), 4.70 (s, 21-H), 3.65 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.25 (m, 6-, 15-H), 3.19–3.04 (m, 4 OH, 2-, 5-, 7-, 14-, 16-, 19-H), 2.74 (t, 4-, 9-, 12-, 17-H), 1.80 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a} = J_{3a,4} = 7.5$, $J_{2,6} = J_{5,6} = 10$, $J_{3a,3s} = 15$, $J_{4,5} = 9.5$. – ^{13}C NMR ($CDCl_3$): δ = 140.5 (C-22), 128.1 (C-24), 126.8 (C-23), 126.7 (C-25), 104.8 (C-1, -20), 97.0 (C-10, -11), 65.8 (C-21), 59.2 (C-6, -15), 58.1 (C-4, -9, -12, -17), 58.0 (C-5, -16), 53.5 (C-2, -7, -14, -19), 35.7 (C-3, -8, -13, -18). – MS (EI) (%) = 508 (12) [M^+], 417 (20), 91 (100).

1,10,11,20-Tetramethoxynonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane (**43**): A solution of **41** (100 mg, 0.28 mmol) in dry THF (10 ml) is stirred at room temp. with NaH (13 mg, 0.56 mmol) and methyl iodide (80 mg, 0.56 mmol) to total conversion (TLC control, 36–48 h). Excess of NaH is cautiously destroyed with H_2O/THF, then the mixture is diluted with H_2O (100 ml) and extracted exhaustively with CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), filtered over a short pad of silica gel and the filtrate concentrated in vacuo. The slightly yellowish residue is

crystallized from CH_2Cl_2/ether to give colorless crystals, m.p. 249–250°C (101 mg, 94%). – IR (KBr): $\tilde{\nu}$ = 3048, 2960, 2932, 2840 (C-H) cm^{-1}. – ^1H and ^{13}C-NMR ($CDCl_3$): Figure 3. – MS (EI): *m/z* (%) = 385 (30) [M^+ + 1], 384 (100) [M^+], 369 (64), 353 (80).

$C_{24}H_{32}O_4$ (384.5) Calcd. C 74.97 H 8.39
Found C 74.87 H 8.31

1,10,11,20-Tetrakis(benzyloxy)nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane (**44**): A solution of **42** (100 mg, 0.19 mmol) in dry THF (50 ml) is stirred with NaH (9 mg, 0.38 mmol) and benzyl bromide (65 mg, 0.38 mmol) in an inert atmosphere at 60°C to total conversion (12–48 h, TLC control). Excess of NaH is cautiously destroyed with wet THF and the mixture diluted with H_2O (200 ml) and then extracted exhaustively with CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), filtered through a short pad of silica gel to remove an excess of benzyl bromide, and the filtrate is concentrated in vacuo to give **44** (119 mg, 88%), colorless crystals, m.p. 196–198°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 3056, 3020, 2944, 2900, 2852 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.36 (m, 23-H), 7.28 (m, 24-H), 7.21 (m, 25-H), 4.72 (s, 21-H), 3.62 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.25 (m, 5-, 6-, 15-, 16-H), 3.16 (m, 2-, -4, 7-, 9-, 12-, 14-, 17-, 19-H), 1.88 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7.5, $J_{3a,3s}$ = 15. – ^{13}C NMR ($CDCl_3$): δ = 140.6 (C-22), 128.1 (C-24), 126.8 (C-23), 126.8 (C-25), 104.9 (C-1, -10, -11, -20), 65.8 (C-21), 59.4 (C-5, -6, -15, -16), 53.7 (C-2, -4, -7, -9, -12, -14, -17, -19), 36.5 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 597 (24) [M^+ – $CH_2C_6H_5$], 91 (100).

1,20-Dimethoxynonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane (**48**): A solution of **27** (50 mg, 0.17 mmol) in dry THF (10 ml) is stirred with NaH (12 mg, 0.51 mmol) and CH_3I (72 mg, 0.51 mmol) at room temp. to total conversion (ca. 12 h, TLC control). Excess of NaH is cautiously destroyed with wet THF, the mixture is diluted with H_2O (200 ml) and exhaustively extracted with CH_2Cl_2. The organic phase is repeatedly washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo to give colorless crystals (53 mg, 97%), m.p. 211–213°C (ether). – IR (KBr): $\tilde{\nu}$ = 3040, 2928, 2810 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.38 (s, OCH_3), 3.31 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.18 (m, 6-, 15-H), 3.15 (m, 10-, 11-H), 3.00 (m, 5-, 16-H), 2.94 (m, 2-, 7-, 14-, 19-H), 2.75 (m, 4-, 9-, 12-, 17-H), 1.71 (dt, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7.5, $J_{3s,3a}$ = 15, $J_{3a,4}$ = 7.5. – ^{13}C NMR ($CDCl_3$): δ = 104.9 (C-1, -20), 64.7 (C-5, -16), 59.6 (C-6, -15), 52.2 (C-2, -7, -14, -19), 51.2 (C-10, -11), 50.8 (OCH_3), 47.4 (C-4, -9, -12, -17), 35.6 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 324 (20) [M^+], 309 (30) [M^+ – OCH_3], 262 (100).

$C_{22}H_{28}O_2$ (324.5) Calcd. C 81.44 H 8.70
Found C 81.30 H 8.74

11,22-Dioxaundecacyclo[13.7.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]docosane (**54**): A solution of **3** (100 mg, 0.38 mmol) in CH_2Cl_2 (10 ml) is stirred with *m*-chloroperbenzoic acid (157 mg, 0.91 mmol) at room temp. for 2 h. Then it is washed with sodium thiosulfate solution (10%) and with $NaHCO_3$ solution (10%), dried ($MgSO_4$), and concentrated in vacuo. By ^1H-NMR and TLC analysis, a byproduct is detected (5%, identified as **25**) which can be separated by crystallization or chromatography from bisepoxide **54** (95%), m.p. 330°C (dec.). The formation of **25** cannot be avoided completely by buffering the reaction solution with NaOAc, but by use of benzoylperoxycarbamic acid in place of *m*CPBA. – **54**: IR (KBr): $\tilde{\nu}$ = 3000, 2920, 2845 (C–H) cm^{-1}. – ^1H and ^{13}H NMR ($CDCl_3$): Figure 5. – MS (EI): *m/z* (%) = 292 (100) [M^+].

$C_{20}H_{20}O_2$ (292.4) Calcd. C 82.16 H 6.89
Found C 82.04 H 6.84

11,11,22,22-Tetrachloroundecacyclo[13.7.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]docosane (**55**): A mixture of **3** (100 mg, 0.38 mmol), TEBA-Cl (50 mg), aqueous KOH (50%, 10 ml), $CHCl_3$ (1 ml), and CH_2Cl_2 (50 ml) is stirred at room temp. to total conversion (36–48 h, TLC control). After a few min the solution becomes opaque, and the product settles in a microcrystalline form. The precipitate, not sufficiently soluble in any solvent, is separated by centrifugation, washed with H_2O/CH_2Cl_2 to remove KOH and TEBA-Cl, and dried in vacuo (10^{-2} Torr/80°C) to give **55** (155 mg, 95%) as a colorless powder, m.p. >330°C. Because of its low solubility, a NMR measurement is not possible. – IR (KBr): $\tilde{\nu}$ = 3030, 2930, 2890, 2860, 2840 (C–H) cm^{-1}. – MS (CI, CH_4): *m/z* (%) = 427 (6) [M^+ + H], 425 (12) [M^+ – H], 423 (8), 393 (32), 392 (26), 391 (100), 390 (32), 389 (98).

Undecacyclo[13.7.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]docosane (**56**): Na (10 g) is added in small pieces to a refluxing suspension of **55** (300 mg, 0.71 mmol) in a mixture of dry THF (50 ml) and *tert*-butyl alcohol (15 ml) under N_2. After 36 h, excess of Na is cautiously destroyed with ethanol/H_2O and the mixture extracted with CH_2Cl_2. The organic phase is washed with H_2O, dried ($MgSO_4$), concentrated in vacuo and the slightly yellowish residue filtered over a short pad of silica gel to give colorless crystals (200 mg, 98%), m.p. >330°C (ether). For the elemental analysis, a sample is purified by sublimation in vacuo (1 Torr/160°C). – IR (KBr): $\tilde{\nu}$ = 3020, 2950, 2900, 2840 (C–H) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): Figure 5. – ^{13}C NMR ($CDCl_3$): Figure 5. – MS (EI): *m/z* (%) = 288 (100) [M^+].

$C_{22}H_{24}$ (288.4) Calcd. C 91.61 H 8.39 Found C 91.49 H 8.44

Dimethyl 11,22-Dioxaundecacyclo[13.7.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]docosane-syn-3,syn-8-dicarboxylate (**57**): A solution of **8** (101 mg, 0.27 mmol) in CH_2Cl_2 (10 ml) is heated with benzoylperoxycarbamic acid (180 mg, 1.0 mmol) to 35°C for 2 h. Then it is concentrated in vacuo (0.5 Torr/100°C). The residue is crystallized from CH_2Cl_2/ether to give **57** (105 mg, 95%), m.p. 215–218°C. – IR (KBr): $\tilde{\nu}$ = 2940 (C–H), 1725 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.78 (s, 2 OCH_3), 2.92–2.95 (m, 2-, 3*a*-, 4-, 7-, 8*a*-, 9-H), 2.87 (m, 5-, 6-H), 2.72 (m, 16-, 17-H), 2.50 (m, 13-, 15-, 18-, 20-H), 2.07 (d, 14*s*-, 19*s*-H), 1.49 (dt, 14*a*-, 19*a*-H); $J_{13,14a}$ = 6.0, $J_{14a,14s}$ = 15.0 Hz. – ^{13}C NMR ($CDCl_3$): δ = 172.8 (C=O), 85.2 (C-1, -10, -12, -21), 64.5 (C-16, -17), 62.3 (C-5, -6), 52.1 (OCH_3), 50.5 (C-3, -8), 44.4 (C-2, -4, -7, -9, -13, -15, -18, -20), 32.1 (C-14, -19). – MS (EI): *m/z* (%) = 408 (18) [M^+], 377 (100), 344 (40).

11,22-Dioxaundecacyclo[13.7.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]docosane-3,8-dione (**58**): A mixture of **13** (160 mg, 0.55 mmol), *m*-chloroperbenzoic acid (85%, 240 mg, ca. 1.2 mmol), and NaOAc (100 mg, ca. 1,2 mmol) in $CHCl_3$ (5 ml) is stirred at ambient temp. for 2.5 h, then heated under reflux for 16 h. The mixture is diluted with CH_2Cl_2 and washed with 10% $Na_2S_2O_3$ and 10% $NaHCO_3$ solutions. The organic phase is dried ($MgSO_4$) and evaporated to give a colorless solid residue which is chromatographed on silica gel with 2% EtOAc/CH_2Cl_2. **58** (170 mg, 96%) is isolated as a colorless crystalline solid, m.p. >330°C. – IR (KBr): $\tilde{\nu}$ = 2950, 2925, 2875 (C–H), 1725 (C=O) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.22 (m, 6-, 22-H), 3.15 (m, 16-, 17-H), 3.00 (m, 2-, 4-, 7-, 9-H), 2.70 (m, 13-, 15-, 18-, 20-H), 2.59 (d, 14*s*-, 19*s*-H), 1.76 (dt, 14*a*-, 19*a*-H); $J_{13,14a}$ = $J_{14a,15}$ = $J_{18,19a}$ = $J_{19a,20}$ = 7.0, $J_{14a,s}$ = $J_{19a,s}$ = 15.0. – ^{13}C NMR ($CDCl_3$): δ = 208.7 (C-3, -8), 85.4 (C-1, -10, -12, -21), 66.8 (C-16, -17), 54.6 (C-2, -4, -7, -9), 50.8 (C-6, -22), 45.1 (C-13, -15, -18, -20), 31.9 (C-14, -19). – MS (EI): *m/z* (%) = 321 (23) [M^+ + 1], 320 (100) [M^+].

21-Oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane (**60**) (cf. **58**): A solution of **4** (100 mg, 0.38 mmol) in CH_2Cl_2 (20 ml) is stirred with *m*-chloroperbenzoic acid (79 mg, 0.46 mmol) and NaOAc as buffer at room temp. for 24 h. After workup

colorless crystals are obtained, m.p. 226–227°C (ether). – IR (KBr): $\tilde{\nu}$ = 3020, 2920, 2845 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): Figure 5. – ^{13}C NMR (C_6D_6): Figure 5. – MS (EI): *m/z* (%) = 278 (100) [M^+].

21,21-Dichlorodecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane (**61**): A solution of **4** (104 mg, 0.4 mmol) in CH_2Cl_2 (20 ml) is stirred with a mixture of KOH (50%, 10 ml), TEBA-Cl (100 mg), and $CHCl_3$ (49 mg, 0.41 mml) at room temp. for 24 h. CH_2Cl_2 (100 ml) and H_2O (100 ml) are added, and the organic phase is separated, washed twice with H_2O and dried ($MgSO_4$). TLC control shows two products which are separated by column chromatography (silica gel, petrol ether) and identified as **61** (121 mg, 92%), m.p. 258–260°C, and **65** (8 mg, 5%). – **61**: IR (KBr): $\tilde{\nu}$ = 3040, 2920, 2850 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.30 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.26 (m, 10-, 11-H), 3.03 (m, 5-, 16-H), 2.83 (m, 4-, 6-, 9-, 12-, 15-, 17-H), 2.67 (t, 2-, 7-, 14-, 19-H), 1.64 (dt, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = $J_{2,6}$ = 6.5, $J_{3a,3s}$ = 15, $J_{4,5}$ = $J_{5,6}$ = 9. – ^{13}C NMR ($CDCl_3$): δ = 81.8 (C-21), 70.0 (C-6, -15), 63.8 (C-5, -16), 52.3 (C-1, -20), 51.9 (C-10, -11), 48.4 (C-2, -7, -14, -19), 47.5 (C-4, -9, -12, -17), 34.1 (C-3, -8, -13, -18). – MS (CI, CH_4): *m/z* (%) = 345 (10), 343 (9), 311 (34), 309 (100); MS (EI): 344 (4) [M^+ +], 311 (34), 309 (100), 273 (77).

Decacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane (**62**): A solution of **61** (50 mg, 0.14 mmol) in dry THF (20 ml) is heated with *tert*-butyl alcohol (3 ml) and finely distributed Na (200 mg) to reflux for 24 h. Excess of Na is cautiously destroyed with EtOH/H_2O, then H_2O (100 ml) und CH_2Cl_2 (100 ml) are added, the organic phase is dried ($MgSO_4$) and filtrated over a short pad of silica gel. Concentration in vacuo gives **62** (38 mg, 96%) as colorless crystals, m.p. 295–298°C. – IR (KBr): $\tilde{\nu}$ = 3010, 2950, 2900, 2880, 2840 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.26 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.24 (m, 10-, 11-H), 3.00 (m, 6-, 15-H), 2.76 (m, 4-, 5-, 9-, 12-, 16-, 17-H), 2.26 (t, 2-, 7-, 14-, 19-H), 1.47 (ddd, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7, $J_{3a,3s}$ = 14. – ^{13}C NMR ($CDCl_3$): δ = 67.7 (C-6, -15)*, 64.5 (C-5, -16)*, 52.7 (C-10, -11), 50.1 (C-2, -7, -14, -19), 47.0 (C-4, -9, -12, -17), 37.1 (C-21), 34.9 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 276 (100) [M^+].

$C_{21}H_{24}$ (276.4) Calcd. C 91.25 H 8.75 Found C 91.14 H 8.79

Dimethyl 21-Oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane-syn-3, syn-8-dicarboxylate (**63**): A solution of **9** (50 mg, 0.13 mmol) and benzoylperoxycarbamic acid (29 mg, 0.16 mmol) in CH_2Cl_2 (4 ml) is stirred at room temp. for 5 h. The mixture is filtered over a short pad of silica gel and the filtrate concentrated in vacuo (0.4 Torr/100°C) to give **63** (51 mg, 100%), colorless crystals, m.p. 221–223°C. – IR (KBr): $\tilde{\nu}$ = 2935 (C–H), 1725 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.77 (s, 2 OCH_3), 3.56 (m, 10-, 11-H), 3.00–3.24 (m, 4 H), 2.73–2.90 (m, 8 H), 2.36 (m, 3*a*-, 8*a*-H), 2.07 (d, 13*s*-, 18*s*-H), 1.56 (dt, 13*a*-, 18*a*-H); $J_{13a,13s}$ = 16.5. – MS (EI): *m/z* (%) = 394 (100) [M^+], 334 (24).

21,21-Dichlorodecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane-3,8-dione (**64**): A standard procedure for carbene addition (Zn/Ag couple, CH_2I_2, DME, room temp./ 16 h) leaves **14** unchanged. Dichlorocarbene addition as described for **4** (1.0 equiv. $CHCl_3$, CH_2Cl_2, TEBA-Cl, 50% aq. NaOH, room temp./16 h, 100% conversion) yields **64** and a trace of **66**. – ^1H-NMR ($CDCl_3$): δ = 3.72 (m, 10-, 11-H), 2.88–3.33 (m, 10 H), 2.84 (d, 13*s*-, 18*s*-H), 2.77 (t, 2-, 7-H), 1.86 (dt, 13*a*-, 18*a*-H); $J_{1,2}$ = $J_{2,6}$ = 7.0, $J_{13a,13s}$ = 16.0.

21,21-Dichloro-10-(dichloromethyl)decacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicosane(**65**): cf. **61**; 148 mg (1.25 mmol) of $CHCl_3$. 137 mg (84%) of colorless crystals, m.p. 225–227°C. – IR (KBr): $\tilde{\nu}$ = 3038, 2960 (C–H) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 5.58 (s, 22-H), 3.40–3.30 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.25–3.10 (m, 4 H)*, 2.99–2.85 (m, 4 H)*, 2.75–2.69 (m, 5 H)*, 1.88–1.58 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H). – ^{13}C NMR ($CDCl_3$): δ = 88.4 (C-22), 81.0 (C-21), 73.8 (C-10), 70.4, 70.2 (C-6, -15), 63.5, 62.5 (C-5, -16) 57.4 (C-11), 54.7 (C-9 oder C-17), 52.1, 51.9 (C-1, -20), 49.0, 48.5, 48.4, 48.2, 48.15, 47.7, 46.7 (C-2, -4, -7, -9 oder C-17, -12, -14, -19), 34.8, 34.7, 34.19, 34.17 (C-3, -8, -13, -18). – MS (EI): *m/z* (%) = 392 (36) [M^+ – Cl], 391 (38) [M^+ – HCl], 115 (100); MS (CI, CH_4): 428 (5) [M^+], 427 (7), 393 (90), 391 (100), 357 (71), 355 (93), 321 (37), 319 (28).

$C_{22}H_{22}Cl_4$ (428.2) Calcd. C 61.71 H 5.18 Cl 33.12
Found C 61.89 H 5.22 Cl 33.34

Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-2-carboxamide (**72**): To a solution of **4** (50 mg, 0.19 mmol) in dry CH_2Cl_2 (10 ml) at –30°C is added a solution of chlorosulfonyl isocyanate (CSI, 54 mg, 0.38 mmol) in dry CH_2Cl_2 (10 ml) over a period of 30 min and the mixture kept at this temp. for 3 h. Then at –10°C acetone (10 ml) is added and the mixture added dropwise to an aqueous solution (20 ml) of Na_2SO_3 (3 g). After the addition of CH_2Cl_2 (20 ml) and acetone (20 ml), the mixture is stirred for 1 h, diluted with H_2O (200 ml) and extracted exhaustively with CH_2Cl_2. The organic phase is washed twice with H_2O, dried ($MgSO_4$), and concentrated in vacuo. The brown residue (containing besides the main product (ca. 70%) traces of **4**, at least three byproducts and polymeric material, TLC control) is purified by chromatography (ethyl acetate/CH_2Cl_2, 1:1) to give colorless crystals (35 mg, 60%), m.p. >330°C. According to the NMR analyses the byproducts most probably result from transannular bond formation. – IR (KBr): $\tilde{\nu}$ = 3466, 3338, 3260, 1672, 1627 (C=O) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 5.30 (br. s, NH_2), 2.82 (d, 4*s*-, 14*s*-H), 2.76–2.57 (m, 3-, 6-, 7-, 8-, 15-, 16-, 17-, 20-H), 2.44 (m, 12-H), 2.34 (m, 5-, 13-H), 1.97 (dd, 9*s*-, 19*s*-H), 1.87 (m, 10-, 18-H), 1.48 (dt, 4*a*-, 14*a*-H), .139 (dt, 9*a*-, 19*a*-H); $J_{3,4a}$ = $J_{4a,5}$ = 6, $J_{4a,4s}$ = 13.5, $J_{5,12}$ = 9, $J_{9a,9s}$ = 10.5 Hz. – ^{13}C NMR ($CDCl_3$): δ = 183.5 (CO), 72.3 (C-2), 71.5 (C-1), 70.1 (C-11), 60.0 (C-6, -17), 59.9 (C-7, -16), 54.7 (C-12), 46.3 (C-3, -15), 44.2 (C-10, -18), 41.7 (C-8, -20), 40.0 (C-5, -13), 36.7 (C-9, -19), 34.4 (C-4, -14). – MS (EI): *m/z* (%) = 305 (6) [M^+], 261 (100).

23-Phenyl-21-oxa-22-azadecacyclo[12.6.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tricosa-10,22-diene (**73**): To a solution of **3** (50 mg, 0.19 mmol) and triethylamine (96 mg, 0.95 mmol) in degassed CH_2Cl_2 (10 ml) at room temp. in an inert atmosphere is added in small portions 4-chlorobenzaldoxime (90 mg, 0.57 mmol) with stirring. The solution becomes immediately opaque, and triethylamine hydrochloride begins to precipitate. After total conversion (ca. 12 h, TLC control), **73** is separated from several byproducts by column chromatography (cyclohexane/ethyl acetate, 1:1) as colorless crystals (52 mg, 72%), m.p. >330 °C (ether). – IR (KBr): $\tilde{\nu}$ = 3050, 3016, 2920, 2888 (C–H) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (m, 2 H), 7.39 (m, 2 H), 7.34 (m, 1 H), 3.36 (d, 3*s*-, 13*s*-H)*, 3.32 (d, 8*s*-, 18*s*-H)*, 3.08 (m, 6-, 15-H), 3.05 (m, 7-, 19-H), 3.05 (m, 9-, 17-H)**, 3.00 (m, 4-, 12-H)**, 2.94 (m, 5-, 16-H), 2.84 (m, 8-, 14-H), 1.71 (m, 8*a*-, 18*a*-H)***, 1.69 (m, 3*a*-, 13*a*-H)***; $J_{3a,3s}$ = 14, $J_{5,9}$ = 5, $J_{2,6}$ = $J_{5,6}$ = 10, $J_{8a,8s}$ = 14. – ^{13}C NMR ($CDCl_3$): δ = 161.4 (C-23), 152.0 (C-10)*, 151.8 (C-11)*, 129.3 (1 C), 128.6 (2 C), 127.5 (2 C), 120.8 (C-20), 82.7 (C-1), 61.7 (C-6, -15), 60.9 (C-5, -16), 57.0 (C-7, -19), 52.2 (C-8, -14), 45.9 (C-4, -12)**, 45.8 (C-9, -17)**, 36.5 (C-3, -13)***, 36.2 (C-8, -18)***. – MS (EI): *m/z* (%) = 379 (6) [M^+], 260 (100).

21,22,23,24-Tetrachlorodecacyclo[12.9.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tetracosa-10,21,23-triene (**76**): A solution of **3** (100 mg, 0.38 mmol) and 2,3,4,5-tetrachlorothiophene *S,S*-dioxide (**75**)[64]

(483 mg, 1.9 mmol) in degassed xylene (50 ml) is heated to reflux under a slow stream of N_2. The reaction mixture becomes dark, and after 4 h it is cooled to room temp. whereby the product settles as fine, colorless crystals. Addition of ether (50 ml) and cooling to −20°C provide a further amount of product, which is removed from the mother liquor by filtration and washed repeatedly with ether to give pure **76** (100 mg, 58%) m.p. >330°C. The mother liquor contains ca. 20−30% of **3**, which can be recovered, besides decomposition products. Total conversion needs a larger excess of tetrachlorothiophene dioxide and a longer reaction time (up to 20 equivalents, 24−36 h); the yield, however, is not significantly improved due to increasing decomposition of **76**. − IR (KBr): $\tilde{\nu}$ = 3016, 2984, 2958, 2938, 2880 (C−H) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.23 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.00−2.87 (m, 2-, 4-, 6-, 7-, 9-, 12-, 14-, 15-, 17-, 19-H), 2.78 (m, 5-, 16-H), 1.73 (m, 3*a*-, 8*a*- 13*a*-, 18*a*-H); $J_{3a,3s}$ = 14, $J_{5,6}$ = 10. − MS (EI): *m/z* (%) = 450 (18) [M^+], 415 (100) [M^+ − Cl], 413 (96).

Decacyclo[12.9.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tetracosa-10,21,23-triene (**77**): A solution of **76** (50 mg, 0.11 mmol) in dry THF (10 ml) is heated with finely distributed Na (13 mg, 0.55 mmol) and *tert*-butyl alcohol (2 ml) in an inert atmosphere at reflux for 4 h. Excess of Na is cautiously destroyed with wet THF, then H_2O is added (100 ml) and the mixture extracted exhaustively with CH_2Cl_2. The organic phase is dried ($MgSO_4$) and filtered over a short pad of silica gel. Concentration in vacuo gives a colorless, oxygen-sensitive residue, which is crystallized from ethanol/ether (33 mg, 95%), m.p. 212−213°C. − IR (KBr): $\tilde{\nu}$ = 3040, 3012, 2966, 2920, 2844, 2660 (C−H) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): Figure 7; δ = 5.70 (m, 21-, 24-H), 5.28 (m, 22- 23-H); $J_{21,22}$ = 10.5, $J_{22,23}$ = 3. − ^{13}C NMR ($CDCl_3$): Figure 7. − MS (EI): *m/z* (%) = 312 (100) [M^+].

$C_{24}H_{24}$ (312.5) Calcd. C 92.26 H 7.74 Found C 92.12 H 7.70

Decacyclo[12.9.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tetracos-10-ene (**78**): A solution of **77** (50 mg, 0.16 mmol) in CH_2Cl_2 (20 ml) is stirred with Pd/C (5%, 100 mg) under a slow stream of H_2 at room temp. to total conversion (ca. 12−18 h). The catalyst is removed by filtration, the solution concentrated in vacuo and the colorless residue crystallized from ethanol/ether to give **78** (50 mg, 98%), m.p. 230−232°C. − IR (KBr): $\tilde{\nu}$ = 3022, 2930, 2844 (C−H) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.13 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 2.88 (m, 4-, 9-, 12-, 17-H), 2.82 (m, 5-, 6-, 15-, 16-H), 2.45 (m, 2-, 7-, 14-, 19-H), 1.56 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H), 1.49 (m, 21-, 22-, 23-, 24-H); $J_{2,3a}$ = 7.0, $J_{3a,3s}$ = 13.5, $J_{3a,4}$ = 4. − ^{13}C NMR ($CDCl_3$): δ = 150.9 (C-10, -11), 63.5 (C-1, -20), 61.4 (C-5, -16), 59.5 (C-6, -15), 54.9 (C-2, -7, -14, -19), 45.8 (C-4, -9, -12, -17), 42.1 (C-21, -24), 37.4 (C-3, -8, -13, -18), 16.0 (C-22, -23). − MS (EI): *m/z* (%) = 316 (20) [M^+], 260 (100).

$C_{24}H_{28}$ (316.5) Calcd. C 91.08 H 8.92 Found C 91.20 H 8.86

11-Oxaundecacyclo[13.10.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]pentacosane (**80**): A solution of **78** (50 mg, 0.16 mmol) in CH_2Cl_2 (10 ml) is stirred with benzoylperoxycarbamic acid (58 mg, 0.32 mmol) at room temp. for 12 h, filtered over a short pad of silica gel and concentrated in vacuo. Benzamide is removed by sublimation in vacuo (10^{-2} Torr/60°C). Crystallization from ether gives **80** (48 mg, 92%) as colorless crystals, m.p. 259−261°C. − IR (KBr): $\tilde{\nu}$ = 3022, 2920, 2844 (C−H) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): Figure 7; δ = 1.55 (s, 22-, 23-, 24-, 25-H). − ^{13}C NMR ($CDCl_3$): Figure 7. − MS (EI): *m/z* (%) = 332 (32) [M^+], 276 (40), 275 (100).

11,11-Dichloroundecacyclo[13.10.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}]pentacosane (**81**): A solution of **78** (100 mg, 0.32 mmol) in $CHCl_3$ (10 ml) is heated with aqueous KOH (5 ml) and TEBA-Cl (10 mg) at reflux for 12 h. The mixture is cooled to room temp. and diluted with H_2O (100 ml) and CH_2Cl_2 (100 ml). The organic phase is washed three times with H_2O (50 ml), dried ($MgSO_4$), filtrated over a short pad of silica gel and concentrated in vacuo to give **81** (92 mg, 92%), colorless crystals, m.p. 220−222°C (ether). − IR (KBr): $\tilde{\nu}$ = 3034, 2920, 2838 (C−H) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.37 (d, 3*s*-, 8*s*-, 14*s*-, 19*s*-H), 3.01 (m, 6-, 16-H), 2.84 (m, 5-, 17-H), 2.66 (m, 4-, 9-, 13-, 18-H), 2.63 (m, 2-, 7-, 15-, 20-H), 1.62 (m, 3*a*-, 8*a*-, 14*a*-, 19*a*-H), 1.53 (s, 22-, 23-, 24-, 25-H); $J_{2,3a}$ = 8, $J_{2,6}$ = 10, $J_{3a,3s}$ = 15, $J_{3a,4}$ = $J_{4,5}$ = 6, $J_{5,6}$ = 11.5. − ^{13}C NMR ($CDCl_3$): δ = 81.4 (C-11), 70.5 (C-5, -17), 60.8 (C-1, -21), 60.0 (C-6, -16), 56.0 (C-2, -7, -15-, -20), 52.1 (C-10, -12), 48.6 (C-4, -9, -13, -18), 41.7 (C-22, -25), 34.7 (C-3, -8, -14, -19), 15.5 (C-23, -24). − MS (EI): *m/z* (%) = 399 (4) [M^+], 398 (6), 365 (30) [M^+ − Cl], 363 (92), 307 (100).

Undecacyclo[12.10.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}.0^{21,24}]tetracosa-10,22-diene (**82**): A solution of **77** (20 mg, 0.064 mmol) in degassed cyclohexane (50 ml) is irradiated at room temp. for 15 min with a low-pressure Hg lamp (254 nm). Concentration in vacuo gives **82** (20 mg, 100%), colorless crystals (ethanol/ether), no m.p. up to 310°C, above 240°C brown discoloration. − IR (KBr): $\tilde{\nu}$ = 3092, 3012, 2980, 2928 (C−H) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 6.39 (m, 22-, 23-H), 3.22 (m, 6-H*), 3.18 (d, 3*s*-, 8*s*-H**), 3.08 (d, 13*s*-, 18*s*-H**), 2.88−2.71 (m, 15-H*, 4-, 5-, 9-, 12-, 16-, 17-H), 2.61 (m, 21-, 24-H), 2.46 (dd, 2-, 7-H***), 2.32 (dd, 14-, 19-H***), 1.57 (m, 3*a*-, 8*a*-, 13*a*-, 18*a*-H); $J_{2,3a}$ = 7, $J_{2,6}$ = 9, $J_{3a,3s}$ = 13.5, $J_{5,6}$ = 10, $J_{21,22}$ = 1.5. − ^{13}C NMR ($CDCl_3$): δ = 139.6 (C-22, -23), 68.8 (C-6)*, 65.7 (C-15)*, 61.3 (C-5)**, 61.0 (C-16)**, 55.7 (C-2, -7)*, 54.4 (C-21, -24), 51.2 (C-14, -19)*, 45.8 (C-4, -9)***, 45.6 (C-12, -17)***, 37.8 (C-3, -8)*, 37.8 (C-13, -18)*. − MS (EI): *m/z* (%) = 312 (32) [M^+], 260 (70), 259 (100).

11,24-Dioxatridecacyclo[13.11.0.0^{1,21}.0^{2,6}.0^{4,12}.0^{5,9}.0^{7,21}.0^{10,12}.0^{10,18}.0^{13,17}.0^{16,20}.0^{22,26}.0^{23,25}]hexacosane (**83**): A solution of **82** (20 mg, 0.06 mmol) in CH_2Cl_2 (10 ml) is stirred at room temp. with benzoylperoxycarbamic acid (43 mg, 0.24 mmol) to total conversion (TLC control, 6 h). After filtration over a short pad of silica gel and concentration in vacuo, benzamide is removed by sublimation in vacuo (10^{-2} Torr/60°C). From ether colorless crystals are obtained (21 mg, 96%), m.p. 238−240°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 4.10 (d, 23-, 25-H), 3.52 (m, 6-H), 3.40 (m, 16-H), 3.23 (d, 3*s*-, 8*s*-H), 3.18 (d, 14*s*-, 19*s*-H), 3.13 (t, 2-, 7-H), 2.86 (m, 5-, 17-H), 2.68 (t, 15-, 20-H), 2.49 (d, 22-, 26-H), 2.44 (m, 4-, 9-, 13-, 18-H), 1.55 (m, 3*a*-, 8*a*-, 14*a*-, 19*a*-H); $J_{2,3a}$ = 8, $J_{2,6}$ = 9, $J_{3a,3s}$ = 14, $J_{3a,4}$ = $J_{4,5}$ = 6, $J_{5,6}$ = 11, $J_{22,23}$ = 4. − ^{13}C NMR ($CDCl_3$): δ = 84.3 (C-10, -12), 68.5 (C-6)*, 66.9 and 66.8 (C-5, -17), 65.6 (C-1, -21), 65.5 (C-16)*, 57.8 (C-22, -26), 57.2 (C-15, -20)**, 56.0 (C-23-, 25), 48.5 (C-2, -7)**, 45.8 and 45.7 (C-4, -9, 13, -18), 34.2 (C-3, -8), 33.8 (C-14, -19). − MS (EI): *m/z* (%) = 344 (18) [M^+], 115 (100).

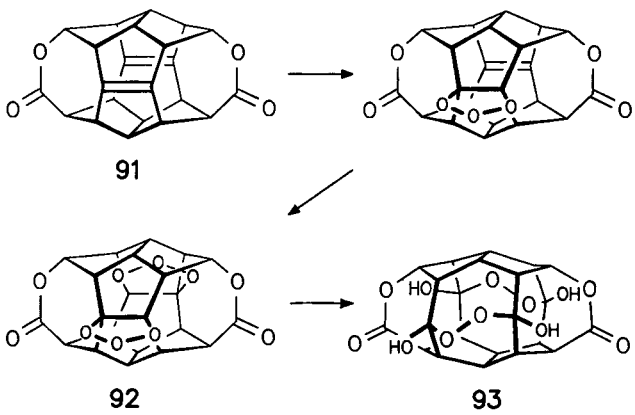
☆ Dedicated to Prof. Dr. *Günther Maier* on the occasion of his 60th birthday

[1] W.-D. Fessner, B. A. R. C. Murty, P. R. Spurr, R. Pinkos, J.-P. Melder, H. Fritz, H. Prinzbach, *Chem. Ber.* **1992**, *125*, 1697 bis 1717, preceding, paper.

[2] P. R. Spurr, B. A. R. C. Murty, W.-D. Fessner, H. Fritz, H. Prinzbach, *Angew. Chem.* **1987**, *99*, 486−488; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 455−456.

[3] G. Szeimies in *Reactive Intermediates* (Ed.: R. A. Abramovitch), Plenum Press, New York, **1983**, vol. 3., p. 299; K. J. Shea, *Tetrahedron* **1980**, *36*, 1683−1715; J. F. Liebman, A. Greenberg, *Strained Organic Molecules*, Academic Press, New York, **1978**; R. Keese, *Angew. Chem.* **1975**, *87*, 568−578; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 528; W. T. Borden, *Chem. Rev.* **1989**, *89*, 1095−1109; P. M. Warner, *ibid.* **1989**, *89*, 1067−1093.

[4] G. Lutz, R. Pinkos, W.-D. Fessner, F. Wahl, G. Rihs, H. Prinzbach, in preparation.
[5] D. Elsässer, K. Hassenrück, H.-D. Martin, B. Mayer, G. Lutz, H. Prinzbach, *Chem. Ber.* **1991**, *124*, 2863–2869.
[6] H. Prinzbach, B. A. R. C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson, *Angew. Chem.* **1987**, *99*, 488–490; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 457–458; G. Lutz, K. Weber, J. Mortensen, J. Heinze, H. Prinzbach, unpublished.
[7] G. K. S. Prakash, V. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc.* **1988**, *110*, 7764–7772.
[8] G. Lutz, Dissertation, Univ. Freiburg, **1990**.
[9] E. Osawa, K. Aigami, Y. Inamoto, *J. Org. Chem.* **1977**, 2621–2626.
[10] G. Sedelmeier, H. Prinzbach, H.-D. Martin, *Chimia* **1979**, *33*, 329–332.
[11] B. A. R. C. Murty, P. R. Spurr, R. Pinkos, C. Grund, W.-D. Fessner, D. Hunkler, H. Fritz, W. R. Roth, H. Prinzbach, *Chimia* **1987**, *41*, 32–36; L. A. Paquette, K. Nakamura, J. W. Fischer, *Tetrahedron Lett.* **1985**, *26*, 4051–4054; L. A. Paquette, K. Nakamura, P. Engel, *Chem. Ber.* **1986**, *119*, 3782–3800; cf. G. Mehta, K. R. Reddy, *J. Org. Chem.* **1987**, *52*, 460–462; G. W. Schriver, T. A. Thomas, *J. Am. Chem. Soc.* **1987**, *109*, 4121–4123.
[12] H. Meier in *Photochemie I, Methoden Org. Chem.* (*Houben-Weyl-Müller*), 4th Ed., **1975**, vol. 4, 5a, p. 257ff.
[13] G. Kaupp, H. Prinzbach, *Helv. Chim. Acta* **1969**, *52*, 956–966.
[14] U. Burkert, N. L. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, DC, **1982**.
[15] W.-D. Fessner, *Dissertation*, Univ. Freiburg, **1986**.
[16] F. Gerson, G. Gescheidt, S. F. Nelson, L. A. Paquette, M. F. Teasley, L. Waykole, *J. Am. Chem. Soc.* **1989**, *111*, 5518–5525.
[17] A. M. de P. Nicholas, D. R. Arnold, *Can. J. Chem.* **1982**, *60*, 2165–2179.
[18] W. F. Maier, P. von R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900; A. B. McEwen, P. von R. Schleyer, *ibid.* **1986**, *108*, 3951–3960.
[19] V. Amir-Erahimi, J. J. Rooney, *J. Chem. Soc., Chem. Commun.* **1988**, 260–261.
[20] Rev.: D. N. Kursanov, Z. N. Parnes, N. M. Loim, *Synthesis* **1974**, 633–651; S. F. Nelsen, M. F. Teasly, *J. Org. Chem.* **1986**, *51*, 3474–3479.
[21] R. Crabtree, *Acc. Chem. Res.* **1979**, *12*, 331–338; K. B. Wiberg, M.-G. Matturo, P. J. Okarma, M. E. Jalon, *J. Am. Chem. Soc.* **1984**, *106*, 2194–2200.
[22] C. J. M. Stirling, *Tetrahedron* **1985**, *41*, 1613–1666; E. K. Garbisch, S. M. Schilderout, D. B. Patterson, C. M. Sprecher, *J. Am. Chem. Soc.* **1965**, *87*, 2932–2944.
[23] W. Luef, R. Keese, *Strained Olefins: Structure and Reactivity of Nonplanar Carbon-Carbon Double Bonds* in *Top. Stereochem.* (Eds.: E. L. Eliel, S. H. Wilen), **1991**, vol. 20, p. 231–318.
[24] R. S. Dewey, E. E. van Tamelen, *J. Am. Chem. Soc.* **1961**, *83*, 3729.
[25] K. J. Shea, A. C. Greeley, S. Nguyen, P. D. Beauchamp, D. H. Aue, J. S. Witzeman, *J. Am. Chem. Soc.* **1986**, *108*, 5901–5908.
[26] G. Lutz, R. Pinkos, B. A. R. C. Murty, P. R. Spurr, W.-D. Fessner, J. Wörth, H. Fritz, L. Knothe, H. Prinzbach, *Chem. Ber.* **1992**, *125*, 1741–1751, following paper.
[27] L. A. Paquette, Y. Miyahara, C. W. Doecke, *J. Am. Chem. Soc.* **1986**, *108*, 1716–1718; L. A. Paquette, Y. Miyahara, *J. Org. Chem.* **1987**, *52*, 1265–1272; L. A. Paquette, J. C. Weber, T. Kobayashi, Y. Miyahara, *J. Am. Chem. Soc.* **1988**, *110*, 8591–8599, and references cited.
[28] J. A. Marshall, H. Faubl, *J. Am. Chem. Soc.* **1970**, *92*, 948–955; N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, K. Aigami, *J. Chem. Soc., Chem. Commun.* **1975**, 372–373; cf. U. Brand, S. Hünig, K. Peters, H. G. v. Schnering, *Chem. Ber.* **1991**, *124*, 1187–1190.
[29] E. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, p. 162, 294.
[30] S. Wolfe, C. F. Ingold, R. U. Lemieux, *J. Am. Chem. Soc.* **1981**, *103*, 938–939; S. Wolfe, C. F. Ingold, *ibid.* **1981**, *103*, 940–941.
[31] For an improved version (MM3) for ketones see N. L. Allinger, K. Chen. M. Rahman, A. Pathiaseril, *J. Am. Chem. Soc.* **1991**, *113*, 4505–4517.
[32] As in ref.[1], nomenclature and numbering of the polycycles have generally been checked with the computer program POLCYC of G. and C. Rücker (*Chimia* **1990**, *44*, 116–120).
[33] B. Albert, D. Elsässer, D. Heckel, S. Kopmeier, H.-D. Martin, B. Mayer, T. J. Chow, T.-K. Wu, S.-K. Yeh, *Chem. Ber.* **1991**, *124*, 803–813, and references cited.
[34] P. H. J. Carlsen, T. Katsuki, V. S. Martin, K. B. Sharpless, *J. Org. Chem.* **1981**, *46*, 3936–3938.
[35] P. F. Schuda, J. L. Phillips, T. M. Morgan, *J. Org. Chem.* **1986**, *51*, 2742–2751; D. Vellemin, *Chem. Ind.* **1986**, 36; F. X. Webster, J. Rivas-Enterrios, R. M. Silverstein, *J. Org. Chem.* **1987**, *52*, 689–691; D. Askin, C. Angst, S. Danishefsky, *ibid.* **1987**, *52*, 622–635.
[36] M. Schröder, *Chem. Rev.* **1980**, *80*, 187–213.
[37] M: Biollaz, W. Haefliger, E. Verlade, P. Crabbe, J. H. Fried, *J. Chem. Soc., Chem. Commun.* **1971**, 1322–1323.
[38] R. Criegee, B. Marchand, H. Wannowins, *Liebigs Ann. Chem.* **1942**, *99*, 550.
[39] E. Höft, S. Ganschow, *J. Prakt. Chem.* **1972**, *314*, 145–156; J. Rebek, R. McCready, S. F. Wolf, A. Mossmann, *J. Org. Chem.* **1979**, *44*, 1485–1493; M. Christl, H. Leininger, P. Kemmer, *Chem. Ber.* **1984**, *117*, 2963–2987.
[40] R. Schwesinger, H. Schlemper, *Angew. Chem.* **1987**, *99*, 1212–1214; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167.
[41] D. J. Sam, H. E. Simmons, *J. Am. Chem. Soc.* **1972**, *94*, 4024–4025; D. G. Lee, V. S. Chang, *J. Org. Chem.* **1978**, *43*, 1532–1536.
[42] A. Fatiadi, *Synthesis* **1987**, 85–127; R. U. Lemieux, E. von Rudloff, *Can. J. Chem.* **1955**, *33*, 170.
[43] J. Tercio, B. Ferreira, W. O. Cruz, P. C. Vieira, M. Yonashiro, *J. Org. Chem.* **1987**, *52*, 3698–3699.
[44] M. Fleischmann, D. Pletcher, *Tetrahedron Lett.* **1971**, 349–350; J. Bertram, J. P. Coleman, M. Fleischmann, D. Pletcher, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 374–381, and references cited; G. J. Edwards, S. R. Jones, J. M. Mellor, *J. Chem. Soc., Chem. Commun.* **1975**, 816–817; T. M. Siegel, L. L. Miller, J. Y. Becker, *ibid.* **1974**, 341–342.
[45] S. Patai, *The Chemistry of Peroxides*, Wiley, New York, **1983**, p. 829; W. Adam, W. J. Baader, *Angew. Chem.* **1984**, *96*, 156–157; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 166.
[46] K. R. Kopecky, P. A. Lockwood, R. R. Gomez, J.-Y. Ding, *Can. J. Chem.* **1981**, *59*, 851.
[47] The product distribution in the ozonolysis of various bissecodienes changes markedly with structural differences: From the bislactone **91** a high yield (ca. 85%) of bis(dihydroxy peroxide) **94** is obtained – evidence for a relatively undisturbed addition of ozone to monoozonide **92** and a "cage-directed" hydrolysis of bisozonide **93**. With parent bissecodiene **3**, in contrast, product formation is unselective supposedly due to transannular bond formation[48].



[48] T. Voss, Diplomarbeit, Univ. Freiburg, **1991**.
[49] D. Cremer, E. Kraka in *Structure and Reactivity* (Ed.: J. F. Liebman, A. Greenberg), VCH, New York, **1988**, chapter 3, and references cited.
[50] K. J. Shea in *Strain and Its Implication in Organic Chemistry* (Ed.: A. deMeijere, S. Blechert), Kluwer Academic Publishing, Dordrecht, **1989**, p. 133–141.
[51] J. Meinwald, S. S. Labana, L. L. Labana, G. H. Wahl, *Tetrahedron Lett.* **1965**, 1789–1793; H. Prinzbach, W. Eberbach, M. Klaus, G. v. Veh, *Chem. Ber.* **1968**, *101*, 4066–4082.
[52] G. Sedelmeier, Dissertation, Univ. Freiburg, **1979**.

[53] L. A. Paquette, T. Kobayashi, *Tetrahedron Lett.* **1987**, *28*, 3531–3534.
[54] E. V. Dehmlow, *Angew. Chem.* **1974**, *86*, 187–196; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 170.
[55] R. B. Woodward, R. Hoffman, *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781.
[56] R. Huisgen, P. Otto, *J. Am. Chem. Soc.* **1968**, *90*, 5342–5343; **1969**, *91*, 5922–5923; L Ghosez, M. J. O'Donnell *Pericyclic Reactions of Cumulenes* in *Pericyclic Reactions*, Academic Press, New York, **1977**, vol. II, p. 79.
[57] J. K. Rasmussen, A. Hassner, *Chem. Rev.* **1976**, *76*, 389–408.
[58] E. W. Della, G. M. Elsey, *Tetrahedron Lett.* **1988**, *29*, 1299–1302.
[59] P. Caramella, P. Grünanger in *1,3 Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), Wiley, New York, **1985**, vol. 1, p. 291.
[60] Appropriately *N*-substituted aziridine rings are valuable protecting groups for highly reactive C,C double bonds in unsaturated dodecahedranes[61]. From several attempts to install such aziridine units at the stage of bissecodienes **3** (and **13**, cf. dioxides **54** and **58**) by dipolar addition of azides[62], no monoadducts **94** and expectedly no bisadducts, but also no aziridines **95** could be secured. Efficient transannular capture of dipolar (diradicaloid) intermediates in the formation or in the fragmentation of triazolines **94** is a plausible explanation. Similar complications are known to govern aziridine annulation to other proximate dienes[51,63].

94

95

[61] K. Weber, H. Prinzbach, unpublished.
[62] P. Scheiner, *Triazoline Decomposition* in *Selective Organic Transformations* (Ed.: B. S. Thyagarajan), Wiley, New York, **1970**, vol. 1, p. 327.
[63] K. Weber, T. Voss, H. Prinzbach, in preparation.
[64] M. S. Raasch, *J. Org. Chem.* **1980**, *45*, 856–867.
[65] P. Bruck, D. Thompson, S. Winstein, *Chem. Ind. (London)* **1960**, 405; P. Bruck, *Tetrahedron Lett.* **1962**, 449–452; W.-D. Fessner, G. Sedelmeier, L. Knothe, H. Prinzbach, *Helv. Chim. Acta*, **1987**, *70*, 1816–1842.
[66] W. P. Weber, *Reactivity and Structure, Concepts in Organic Chemistry, Silicon Reagents for Organic Synthesis*, Springer Verlag, Berlin, **1983**, vol. 14; M. Brossi, C. Ganter, *Helv. Chim. Acta* **1988**, *71*, 848–858.
[67] E. Vogel, W. Grimme, E. Dinné, *Tetrahedron Lett.* **1965**, 391–395; W. G. Dauben, M. S. Kellogg, *J. Am. Chem. Soc.* **1971**, *93*, 3805–3807.
[68] D. A. Shirley, *Org. React.* **1954**, *8*, 28.
[69] For the calculation, the MM2 force field recently parametrized for epoxides was used: B. L. Polgar, D. J. Raber, *J. Org. Chem.* **1984**, *54*, 5032–5035.
[70] Cf. the (calculated) hyperstability of a series of cylindrical polycyclic trienes and trienediones – considered as potential dodecahedrane precursors: S. Lalitha, J. Chandrasekhar, G. Mehta, *Tetrahedron Lett.* **1990**, *31*, 4219–4222.
[71] K. B. Wiberg, R. D. Adams, P. J. Ocarma, M. G. Matturro, B. Segmüller, *J. Am. Chem. Soc.* **1984**, *106*, 2200–2206; cf. R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, L. M. Trefonas, *ibid.* **1974**, *96*, 4342–4343; J. E. McMurry, G. J. Haley, J. R. Matz, J. C. Clardy, G. van Duyne, R. Gleiter, W. Schäfer, D. H. White, *ibid.* **1986**, *108*, 2932.
[72] W. v. E. Doering, J. C. Schmidhauser, *J. Am. Chem. Soc.* **1984**, *106*, 5025–5026.
[73] E. Vogel, *Ber. Dtsch. Chem. Ges.* **1952**, *85*, 25–29; K. B. Becker, *Helv. Chim. Acta* **1977**, *60*, 68–80; K. Kakiuchi, H. Takeuchi, Y. Tobe, Y. Odaira, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1613–1614; N. Takaishi, H. Takahashi, O. Yamashita, Y. Inamoto, *Tetrahedron Lett.* **1986**, *27*, 4862–4865; K. Okada, H. Kawai, K. Okubo, T. Uesogi, M. Oda, *ibid.* **1988**, *29*, 2333–2336; A. Kumar, J. D. Lichtenhahn, S. C. Critchow, B. E. Eichinger, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 5633–5634, and references cited.
[74] O. Ermer, C.-D. Bödecker, *Helv. Chim. Acta* **1983**, *66*, 943–959; L. A. Paquette, C. C. Shen, *J. Am. Chem. Soc.* **1990**, *112*, 1159–1164; and references cited; P. D. Bartlett, A. J. Blakeney, G. L. Combs, J. Galloy, A. A. M. Roof, R. Subramanyam, W. H. Watson, W. J. Winter, C. Wu in *Stereochemistry and Reactivity of Systems Containing π Electrons* (Ed.: W. H. Watson), Verlag Chemie International, Deerfield Beach, FL, **1983**, p. 75; P. D. Bartlett, M. D. Ravenscroft, A. M. Roof, *J. Org. Chem.* **1987**, *52*, 1847–1850, and references cited.

[52/92]

CAS Registry Numbers

1: 89683-62-5 / **3**: 107798-67-4 / **4**: 107798-68-5 / **8**: 119071-69-1 / **9**: 119071-70-4 / **13**: 107819-45-4 / **14**: 107798-69-6 / **17**: 107798-72-1 / **18**: 107798-73-2 / **22**: 118420-87-4 / **24**: 140872-73-7 / **25**: 140901-42-4 / **26**: 118760-94-4 / **27**: 118760-96-6 / **29**: 118760-99-9 / **35**: 140901-43-5 / **36**: 118761-04-9 / **37**: 118761-05-0 / **38a**: 118760-95-5 / **38b**: 140901-44-6 / **38c**: 140901-45-7 / **39**: 118761-03-8 / **41**: 118761-06-1 / **42**: 118761-07-2 / **43**: 118761-12-9 / **44**: 118761-13-0 / **48**: 140901-46-8 / **54**: 107798-77-6 / **55**: 107798-83-4 / **56**: 107819-40-9 / **57**: 119108-85-9 / **58**: 107798-79-8 / **60**: 107798-74-3 / **61**: 107798-80-1 / **62**: 107819-37-4 / **63**: 140901-47-9 / **64**: 107798-81-2 / **65**: 140901-48-0 / **72**: 140925-95-7 / **73**: 140901-49-1 / **76**: 140901-50-4 / **77**: 140901-51-5 / **78**: 140901-52-6 / **80**: 140901-53-7 / **81**: 140901-54-8 / **82**: 140901-55-9 / **83**: 140901-56-0 / 2,3,4,5-tetrachlorothiophene *S,S*-dioxide: 72448-17-0 / 4-chlorobenzonitrile oxide: 15500-74-0