ChemInform Abstract: The Pagodane Route to Dodecahedranes. Scope and Limitation of the Dehydrocyclization Stratagem

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The Pagodane Route to Dodecahedranes Scope and Limitation of the Dehydrocyclization Stratagem☆

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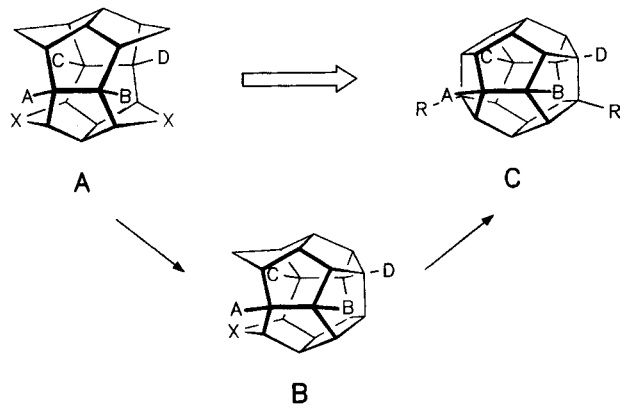
The stepwise route B from pagodanes to dodecahedranes was completed by double catalytic dehydrocyclization of saturated (alkylated) bisseco precursor substrates (**2**, **3**, **5**, **16**). Based on pagodane, dodecahedranes (**9**, **10**, **13**, **14**, **17**) were obtained in up to 53% yield. Transannular C,C bond formation at the bisseco stage and partial (C−alkyl) or total (C−OR, C−CO_2R) removal of substituent groups under the necessarily forcing reaction conditions constituted preparative limitations. Attempts at alternative ring closure methodologies (homo-Norrish type II, homoenolization, carbene insertion) have remained unsuccessful.

The directed transformation of pagodanes into dodecahedranes along the route B[1,2] as originally designed for the parent $C_{20}H_{20}$ hydrocarbons (Scheme 1 in ref.[1]) implies, in principle, only three operations: $2\sigma \rightarrow 2\pi$ opening of the pagodane four-membered ring, hydrogenation of the resulting C=C bonds, and dehydrogenative ring closure. In the two preceding papers, we have presented a highly efficient, broadly applicable protocol for the first operation[1] and a viable circumvention of the complications as caused in the second operation by the strict hyperstability of the bissecododecahedrene intermediates[2]. In this paper, we detail the "scope and limitations" of the route B with respect to the third stage (Scheme 1, **A** → **B** → **C**), where the dehydrocyclization methodology[3] is applied to the formation of the two ultimate C,C bonds.

Scheme 1



Dehydrocyclizations A → B → C

In the Paquette approach to dodecahedranes[4], the missing C,C bond in the seco-precursor substrates (**B** → **C**, X = CH_2) was generated by heterogeneous catalytic dehydrogenation. This methodology, previously elaborated in the oil-refining industry, has recently been reviewed by Schleyer[5] and by McKervey and Rooney[6], especially with respect to the preparative and mechanistic implications in adamantanoid hydrocarbon systems. No doubt, processes of this kind were also involved in our totally catalytic transformation of pagodane into dodecahedrane[5,7].

Due to a lack of activation and poor steric accessibility, the Paquette group had to apply rather vigorous reaction conditions to induce dehydrocyclization in secododecahedranes **B**. Generally, intimate mixtures of substrate and catalyst (Pd/C, up to 100-fold amount) had to be heated to temperatures as high as 250°C for extended periods of time. Presaturation of the catalyst with hydrogen was found to be necessary in order to suppress competing 1,2-dehydrogenation leading to unsaturated, rapidly polymerizing intermediates. Yet, this excess of hydrogen turned out to be a disadvantage insofar as it furthered the reductive elimination of previously introduced functionalities[8]. Later, Pt(0) was proposed as a superior catalyst which seemed to be more tolerant specifically to alkyl substitution[9]. In experiments performed on the 10-mg scale, yields as high as 56% (72%) of pure (methyl)dodecahedrane were thus achieved[4].

As judged naively by the transannular distances between the methylene carbons to be linked and by the steric encumbrance of the hydrogens to be eliminated (Figure 1 in ref.[1]), dehydrocyclization in our bissecododecahedranes (**A** → **B**, X = CH_2) should need comparably drastic conditions as were found necessary by the Paquette group for the ensuing **B** → **C** step, with the consequence that the overall process **A** → **C** would face rather strict preparative complications. Thus, concern was justified about potential side reactions involving the various functionalities A−D. The latter are, at least partly, needed to achieve the satu-

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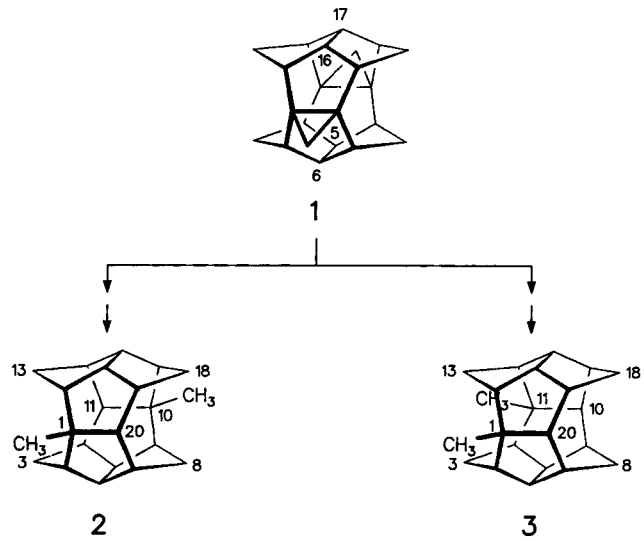
ration of the bissecodiene precursors[2] and are much desired for the ultimate functionalized dodecahedranes. Still, the comparably convenient access to pagodanes[10] made the decision easy to take the risks and to invest time and effort into this dehydrogenative bond-forming approach in spite of its potential pitfalls.

Since the parent saturated **A**-type hydrocarbon (X = CH_2, A–D = H) was not directly accessible[2] and since alkyl substituents were given the best chance to survive dehydrogenative reaction conditions, we first tackled the problem of preparing alkylated bisseco precursors **A** from the readily available cyclopropanated bissecododecahedranes **1** and **4**. Hydrogenolytic fission of annulated small rings, specifically of cyclopropane rings, is an established procedure for the creation of angular methyl groups in cage hydrocarbons[5,6,11].

On the basis of the amount of strain released by hydrogenolysis of **1** or **4**, the scission of the exocyclic cyclopropane bonds to furnish methylbissecododecahedranes **2** (**3**) and **5** was considered much more likely than scission of the sterically inaccessible endocyclic cyclopropane or of the longer "ridge" bonds [C5–C6 (C16–C17) in **1**, C5–C6 (C15–C16) in **4**][12]. Yet, the exocyclic cyclopropane C,C bonds are imbedded in a rather protected environment and thus are not easily accessible to the catalysts. It should be recalled that even the parent [3.3.1]propellane survives 6 h of vigorous hydrogenating conditions[13]. Indeed, it took rather forcing conditions to effect hydrogenolysis in **1** (20-fold amount of 10% Pd/C, 20 atm H_2, 150°C; very slow reaction at 100°C). After complete conversion (6 h) and careful extraction of the catalyst with *n*-hexane, ca. 90% of the material were recovered as a mixture of the C_{2h}-symmetrical 1,10- (**2**) and the C_s-symmetrical 1,11-dimethylbissecododecahedranes (**3**) in a ratio varying between 1:2 and 2:3. Compound **2** could be enriched to a ca. 20:1 ratio by fractional crystallization from benzene/ethanol. The missing 10% of material in the mass balance could not be recovered from the catalyst either by sublimation or by use of more polar solvents.



C_{2h} (C_s) symmetry for **2** (**3**) [*m/z* (%) = 292 (40) (M^+), 277 (100)] followed as a result of six (eight) ^{1}H- and six (seven) ^{13}C-NMR skeletal signals, respectively. Typical of these saturated, more convex bissecododecahedrane skeletons with their longer transannular (d_{C1-C11} = 3.5 Å) and shorter lateral C,C distances (d_{C3-C13} = 3.0 Å), and thus stronger lateral H/H compression as compared to **1** and **4**, are inter alia (Figure 1) the pronounced low-field chemical shift measured for the *syn*-methylene protons (δ = 1.56 in parent pagodane; cf. Figure 2 in ref.[1]) and the size of the geminal and vicinal coupling constants (cf. the H/H interplanary angles in Table 2 of ref.[2]) with e.g. 13.5 Hz for the practically eclipsed "frontal" hydrogens 10(11)/20-H.

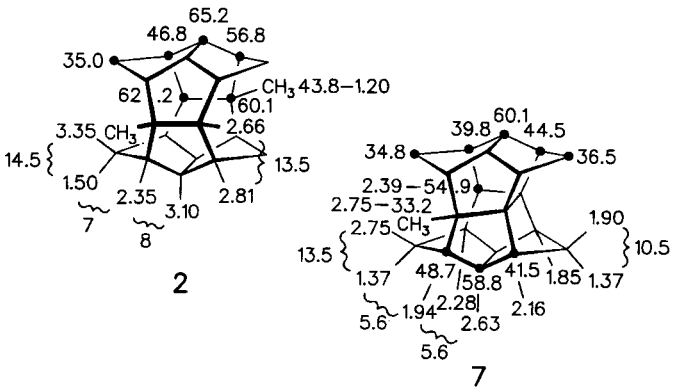
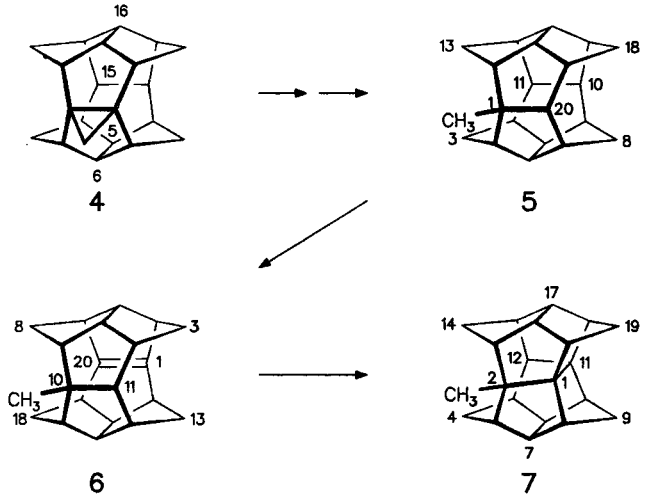


Figure 1. ^{1}H- and ^{13}C-NMR data [$CDCl_3$; δ, *J* (Hz)] of bissecododecahedrane **2** and secopagodane **7**

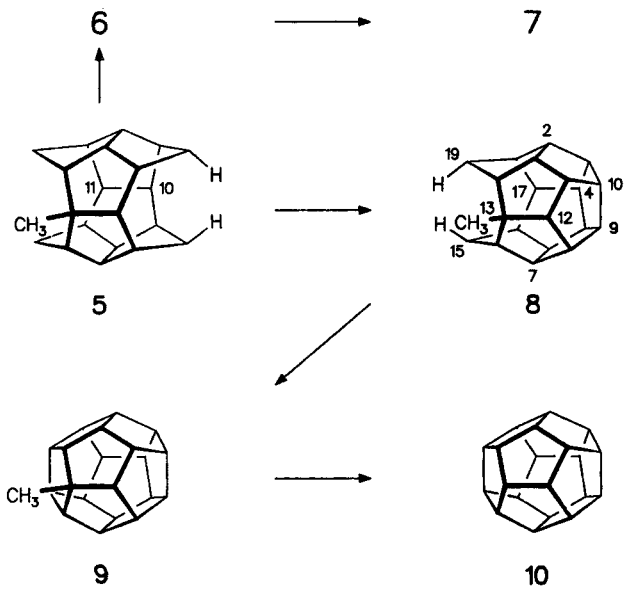
The hydrogenolysis of **4** proceeded less uniformly under various conditions [e.g. intimate mixtures of **4** (40 mg) with Pd/C, Ni/ethyl acetate, PtO_2/ethyl acetate, 30–100 atm H_2; 80–150°C]. The desired hydrocarbon **5** was consistently accompanied by monoene **6**, secopagodane **7**, and several minor components. Prototypical are the results achieved under conditions similar to those applied to **1** (10% Pd/C, 50 atm H_2, 100°C, 1.5 h, >90% conversion). The crude reaction mixture (80–90%) consisted of 70–75% of **5**, 10% each of **6** and **7**, and 5–10% of other compounds (GC/MS). The structural assignments were reliably based on the ^{1}H-NMR spectra (250 MHz, $CDCl_3$) of crude mixtures by evaluating the easily discernible signals for the respective *syn*-methylene and the methyl protons [**4**: *m/z* = 276; δ = 3.28 (d), 0.22 (s); **5**: *m/z* = 278; δ = 3.38 (d, *J* = 15 Hz), 3.27 (d, *J* = 15 Hz), 1.21 (s); **6**: *m/z* = 276; δ = 3.15 (d, *J* = 13.5 Hz), 3.03 (d, *J* = 13.5 Hz), 1.19 (s); **7**: *m/z* = 276; δ = 2.75 (d, *J* = 13.5 Hz), 0.98 (s)]. After a 6-h reaction time (total conversion), the composition of the crude eluate (75–80%) changed to 15% of **5**, 60% of **6**, 20% of **7**, and 5% of other compounds. Clearly, the highly strained saturated bisseco hydrocarbon **5** even under a high pressure of hydrogen readily expels the 10(11)-hydrogen atoms to give the hyperstable olefin **6**, which is the probable precursor of **7**. It should be recalled that in experiments designed for the catalytic hydrogenation of the parent bissecododecahedra(di)enes (**22**, **23**)[2], the analogous 1,2-hydrogen elimination and isomerization at the stage of monoene (cf. **23** → **25**) predominated.

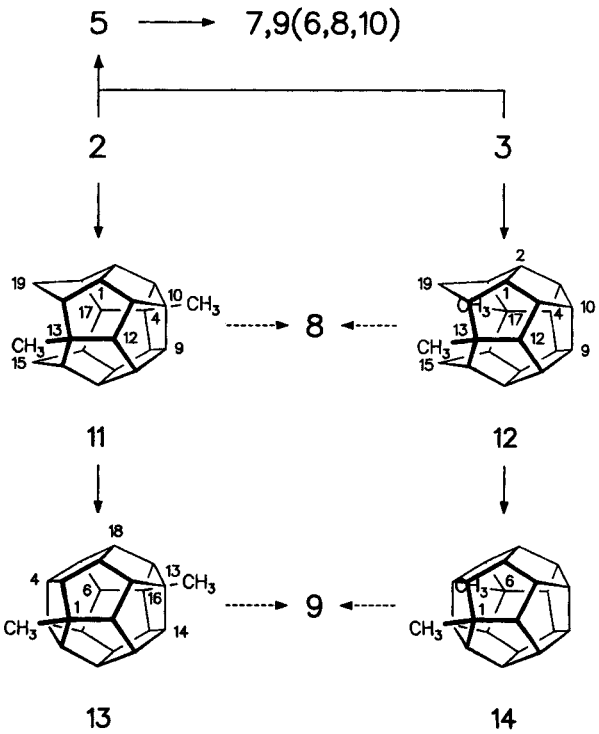
Hydrogen elimination again occurred regiospecifically insofar that no olefin could be found other than **6**, in agreement with the calculated relative stabilities (cf. Table 1 in ref.[2]). Compound **7** was quantitatively obtained after heating of **4** to 300°C for 3 h; its ^{1}H- and ^{13}C-NMR data (Figure 1) nicely reflect the geometrical discrepancies between "open" (left) and "closed" (right) sides[2] of the (seco)pagodane skeleton.



For the double dehydrocyclization of **5** to give methyldodecahedrane (**9**)[14], intimate mixtures of precursor **4** (55 mg) and a 10–100-fold excess of 10% Pd/C, presaturated with H_2 (5 atm), were heated to 250°C. In two prototypical runs with a 10-fold excess of catalyst after a heating time of 3 (5) h and thorough extraction with *n*-hexane (soxhlet, 3 h), the solid extracts (average 50 mg, 90%) were analyzed by GC/MS. In addition to several trace components (each <2%), six fractions were eluted in the following sequence: *m/z* (%) = 276 [20 (21)], 278 [3 (5)], 278 [8 (9)], 280 [0 (3)], 274 [30 (30)], 260 [10 (9)]. By a comparison of the MS fragmentation patterns, the first component with *m/z* = 276 was found to be identical with **7**. The first of the two $C_{21}H_{24}$ hydrocarbons (*m/z* = 278) was assumed to be residual **5**. The last two eluates were obtained in nearly pure state by fractional sublimation (80°C/1 Torr) and were unambiguously identified (^{1}H, ^{13}C NMR) as methyldodecahedrane (**9**) and parent dodecahedrane (**10**)[15]. In parallel with an observation in the catalytic hydrogenation study[2], the $C_{21}H_{28}$ hydrocarbon (*m/z* = 280) is believed to arise from cleavage of a "ridge" C,C bond (C5–C6) in e.g. **5**.

In the dehydrocyclization of **2** and **3**, competitive dehydrogenation, operative in **5**, cannot interfere or can only come into play after demethylation to **5**. After exposing the original 2:3 mixture of **2**/**3** (40 mg) to the standard dehydrogenation conditions (100-fold excess of catalyst) and workup after 6 h (total conversion), 30–34 mg (75–83%) of a crude oily material was extracted which consisted of three main and two trace components (GC/MS): *m/z* (%) = 276 (29), 290 (28), 288 (29), 274 (1), and 288 (1). According to spectral comparison (MS, ^{1}H, ^{13}C NMR), the first was again methylsecopagodane **7**, the third D_{3d}-1,16-dimethyldodecahedrane (**13**)[9,16], the fourth methyldodecahedrane (**9**), and the fifth C_{2v}-1,6-dimethyldodecahedrane (**14**)[9,16]. The structure of the second, overreduced ($C_{22}H_{26}$) component remains unknown. When pure C_{2h} precursor **2** was treated in the same way, workup after 8 h provided an average of 90% of crude material consisting of 25% of **7**, 20% of **13**, 28% of **9**, 11% of parent **10**, and 7% of non-identified components. With 53% of (methyl)dodecahedranes, this was the best result achieved in this series of experiments. In several such runs, **14** was consistently found in much lower yields than **13**. Thus, demethylation en route from **3** to **14** must be relatively efficient. In the optimized Paquette protocol (12-mg scale)[9], **14** had been prepared from the 4,12-

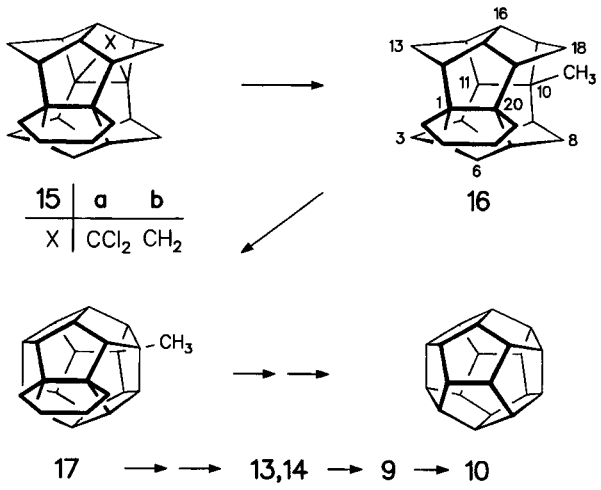




dimethyl analog of **12** ($d_{H15-H19}$ = 1.95, $d_{C15-C19}$ = 3.03 Å)[16] in 74% yield along with 10–15% of **9**.

In the evaluation of these results, the point must be stressed that in experiments performed under identical conditions the total yield of dodecahedranes has been reproduced with some accuracy (±5%) whilst the relative portions of the individual members [**9**, **10**, **14** (**15**)] varied significantly. It is understood that yields and product distribution in such solid-phase catalytic reactions depend on seemingly trivial aspects such as size, preparation, and homogeneity of a sample and were therefore difficult to reproduce precisely. Not the least for this reason, it was tempting to make the respective reaction mixtures more uniform by complete dealkylation and thus to reduce the isolation procedure to the separation of **7** (**25**) and **10**. From the body of experimental data, a certain kinetic selectivity in the demethylation seemed to be deducible which was fast in the sequence starting from **3** but very slow for **7**. In fact, similar differences in the rate of dealkylation, presumably due to differences in steric accessibility to the catalyst, had been preparatively exploited for the regioselective demethylation of 1,3,16-trimethyldodecahedrane[9]. Our conditions applied here to the demethylation of the (di)methyldodecahedranes are conceivably not yet optimal. In the adamantane series, methyl groups can be very efficiently removed by passing the substrates over a nickel/alumina catalyst in an H_2 atmosphere[5,6,8]. The potential of such vapor-phase techniques was, however, not explored further, as progress on alternative tracks promised a far more expeditious access to **10** (see Summary).

By extrapolating the behavior of 1,10-dialkylated bisseco structures of type **2** under dehydrocyclization conditions, one can expect an even more selective formation of the dodecahedrane nucleus for 1,10,11(20)-tri(tetra)alkylated bisseco precursors. A trisubstituted example, the methylcyclohexano derivative **16**, was readily prepared from the dichlorocyclopropa compound **15a**[2] by conventional dehalogenation (Na, *tert*-butyl alcohol, THF, 97%) and exposure of the product **15b** to the proven hydrogenolytic conditions (5% Pd/C, 50 atm H_2, 150°C, 2 h). Aside from 93% of **16**, a trace of parent dodecahedrane **10** (<2%) was detected by its characteristic ^{1}H- and ^{13}C-NMR resonance lines. The ^{1}H- and ^{13}C-NMR spectra of **15b** and **16**, in the latter case completely assigned with the help of COSY experiments (Figure 2), revealed the expected close analogies with the data presented for **15a**[2] and e.g. for **2** (Figure 1). In the case of **16**, with δ = 3.44 (J = 15 Hz), the 8*s*(18*s*)-H low-field shift [cf. 2*s*(13*s*)-H: δ = 3.32] is even more pronounced than that of δ = 3.35 for **2**, indicative of an even stronger transannular H/H compression at a shorter distance. According to the MS fragmentation pattern [m/z (%) = 332 (24) [M^+], 276 (34), 275 (100)], the radical cation of **16** loses preferably the C_4 portion of the cyclohexane ring. Because of limited supply of material, only two orienting dehydrogenation experiments could be performed with **16** (5-mg scale, tenfold excess of 10% Pd/C, 2 atm H_2, 280°C, 4 h). GC/MS analysis of the hexane extract (ca. 3 mg of colorless solid) revealed one main (ca. 30%; m/z = 328)



and several small components with molecular masses between 273 and 328, as well as one (2–3%) with m/z = 260 (**10**). The MS fragmentation pattern of the main component with m/z (%) = 328 (100) [M^+], 313 (16), 300 (15), 287 (17), 273 (32), 260 (14) was fully supportive of its expected methylcyclohexanododecahedrane structure **17**. The ^{1}H-NMR spectrum consisted mainly of signals in the expected range of δ = 2.8–3.5 without, however, allowing a more detailed interpretation. The cyclohexanotriquinane part of **17** has recently been considered a building block for the construction of dodecahedranes[17].

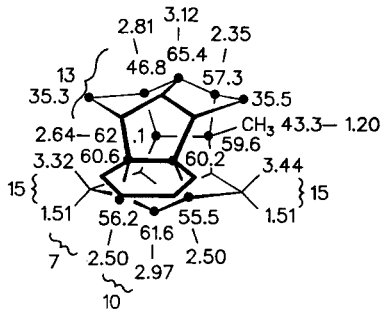
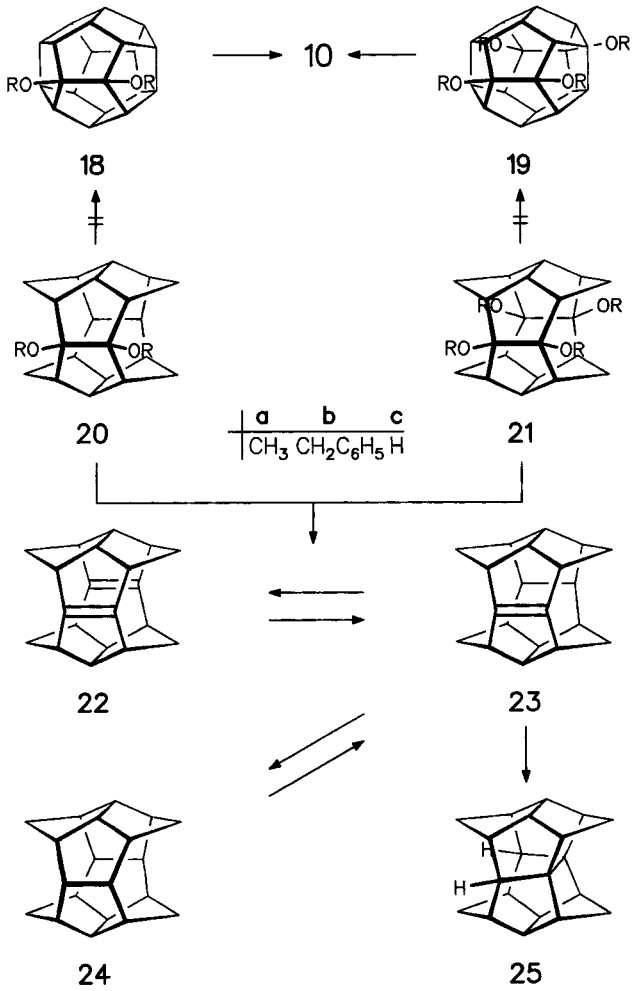


Figure 2. ^{1}H- and ^{13}C-NMR data [$CDCl_3$, δ, J (Hz)] of cyclohexanobissecododecahedrane **16**

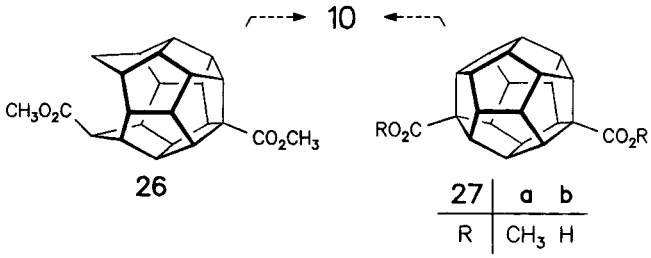
Aiming at dodecahedranes **C** with functionalities (A–D) other than alkyl groups, we next studied OR substituted derivatives of type **A**, specifically **20a–c** and **21a–c**, in full knowledge of the risk involved in the survival of such relatively weakly bound substituents. Under various hydrogenation as well as dehydrogenation conditions (10% Pd/C, 1–14 atm H_2, 170–250°C, 1–5 h), generally no dodecahedranes (**18**, **19**, **10**) were formed. In each case, the RO groups were completely stripped off before cyclization took place to deliver the parent secopagodane **25** as the exclusive product (>90% isolated). Hopes to essentially prevent the elimination of the functionalities by making use of the calcium salts of the *vic*-diol groups in **20c** or **21c** did not materialize. Under the necessarily forcing reaction conditions, again only **25** was isolated (85%). In the benzyl ethers **20b** and **21b**, under mild hydrogenation conditions (CH_2Cl_2,

Pd/C, 1 atm. H_2, room temperature), cleavage could be restricted to the *O*-benzyl bonds to provide the known diol **20c**[1] and the only sparingly soluble (and therfore not fully characterized) tetrol **21c**, respectively, in quantitative yields. That again only **25** and not even trace amounts of the still elusive parent bissecododecahedrane **24** could be observed when **20a** was exposed to hydrogenating conditions can be taken as another manifestation of the high propensity of **24** to lose hydrogen with formation of the hyperstable **23**, a proven precursor of **25**[2].



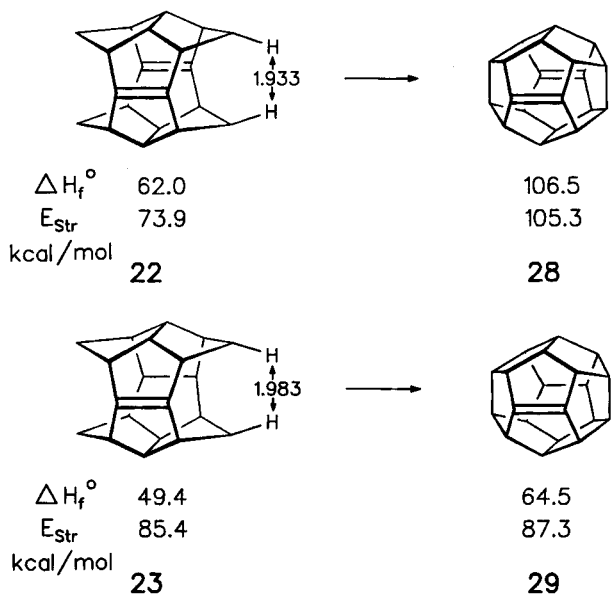
Within the context of substituent stability during the dehydrocyclization procedure, more recent findings have provided pertinent information. From the seco diester **26**, prepared according to the S_N2 route from functionalized pagodanes[18], under no set of dehydrogenating conditions could any dodecahedrane diester **27a**, known from an independent route[19], be procured. From the catalyst, only ca. 30% of material were eluted (hexane, ethyl acetate), which contained ca. 3% (GC/MS) of the parent dodecahedrane **10**. Similar treatment of **27a**[19] provided **10** in 35% isolated yield.

At this stage, strict limitations had been obviously set by the dehydrocyclization strategy for potential shortcuts in the route B which consist in direct transformations of the



unsaturated bisseco structures **22/23**, introduced above as likely intermediates en route from **20/21** to **25**, into the unsaturated dodecahedranes **28/29** (Scheme 2, see ref.[1] for comments on the reliability of the energy data). On account of the larger distances between the lateral *syn*-hydrogen atoms to be removed as well as the highly unfavorable energetic changes involved as compared to the saturated systems **A/C**, such transformations were given a priori little chance. According to our previous experience with diene **22**, the H_2-presaturated catalyst should cause at least partial hydrogenation to **23**[2] and then induce transannular bond formation in the latter to yield **25**. For experimental verification, we elucidated the fate of diene **22** and monoene **23** in the standard dehydrocyclization procedure (5 mg, 10% H_2-saturated Pd/C, 250°C, 4 h) and proved our premise to be correct indeed. Consistent with a rapid hydrogenation **22** → **23** and isomerization **23** → **25**, in both cases **25** was the exclusively observed monomeric product, isolated in higher than 60% yield. Since we learnt in the meantime that under these conditions the highly strained unsaturated dodecahedranes **28** and **29**[20] become rapidly saturated to give **10**, the latter's absence in these experiments makes any cyclizations **22** → **28** or **23** → **29** highly improbable.

Scheme 2

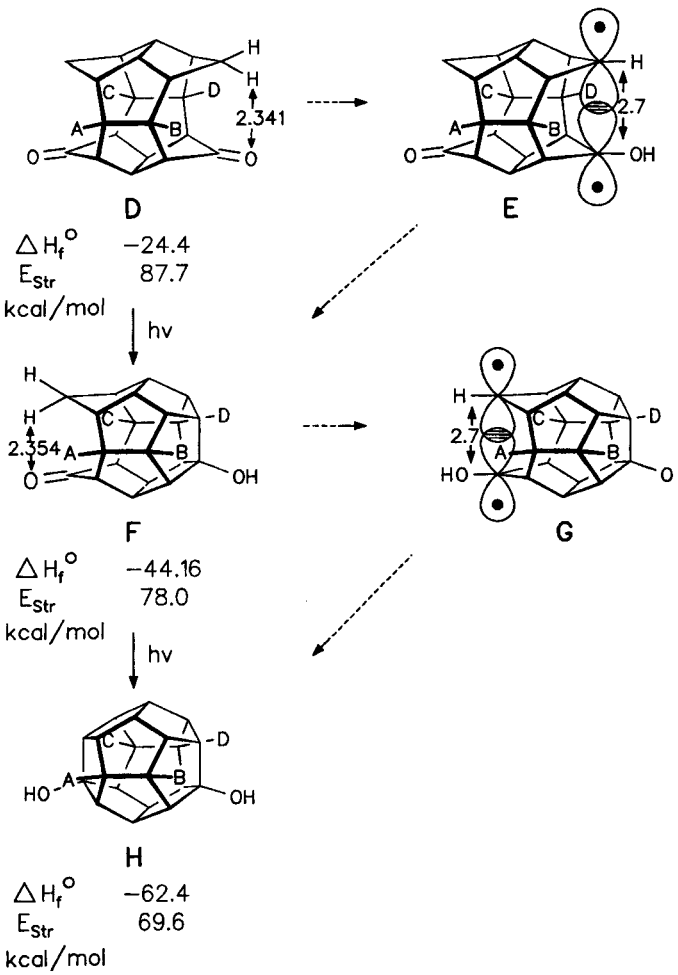


Alternatives to the Dehydrocyclization Stratagem

Pagodane-4,9-dione (**A**, X = CO; A–D = H), conveniently accessible by the original pagodane synthesis[10], is the

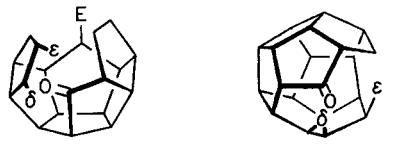
starting material for several saturated and unsaturated bisseco diones of type **D** (Scheme 3)[2]. From the carbonyl functionalities, help in the formation of the two missing lateral C–C bonds was sought by application of methodologies which would better tolerate the respective substitution patterns (A–D). For this purpose, techniques such the homo-Norrish-type II reaction[21], homoenolization[22], and carbene insertion[23] were selected.

Scheme 3



Double homo-Norrish-type II cyclization **D** → **F** → **H**, at first sight, appeared highly attractive. It would be applicable to even strongly endothermic transformations and would tolerate a great variety of functionalities in the participating compounds. In fact, this photochemical reaction played a key role in the Paquette synthetic scheme, for example in the regiospecific cyclizations of the ketones **I** and **K**. As can be learned from the data calculated (MM2) for the parent structures **D/F/H** (A–D = H)[24], both cyclization steps are energetically favorable and the transannular H–O distances in **D** and **F** lie well below the critical limit[25]. At distances of only ca. 2.7 Å between opposite C,C radical centers in **E/G**, an effective C,C bond formation seemed to be guaranteed.

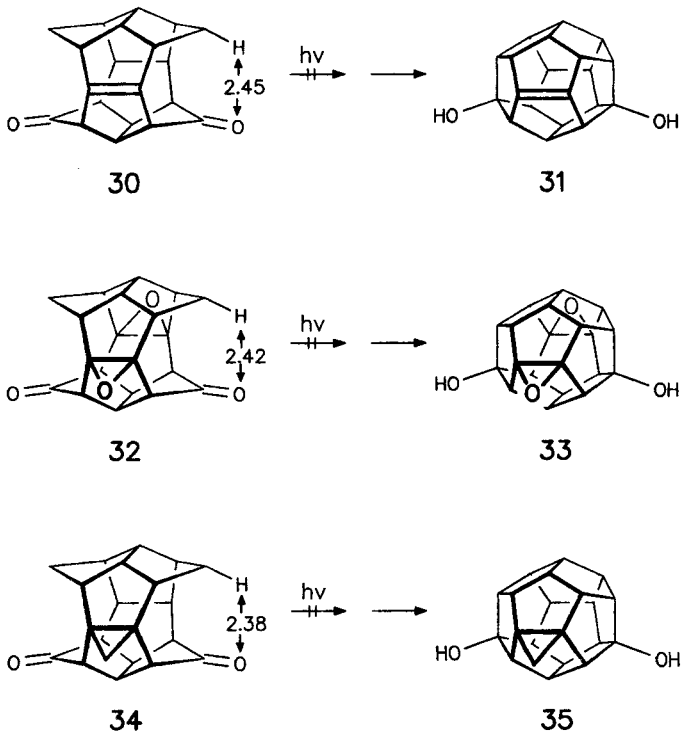
However, the H–O distance is not the only criterion for efficient H abstraction. To provide an optimal transition-state geometry ("in plane n-orbital mechanism"[26]), the hydrogen atom to be attacked should be situated close to the half-filled n-orbital of the oxygen atom at an angle normal to the C=O double bond. More precisely, the angles Δ and τ as defined by Scheffer[27] should lie between 90–120 and near 0°, respectively. For comparison, the respective angles in ketones **I** and **K** were computed (MM2)[25], and on this basis it is clear that only the δ hydrogens [d_{O-H} = 2.37 (2.40) Å] are abstracted.



I	Hδ	Hε
Δ(°)	107	90
τ (°)	30	86

K	Hδ	Hε
	101	76
	47	70

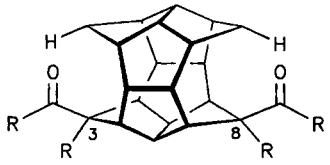
The high expectations that we originally had associated with this photochemical methodology, specifically with the twofold cyclization in the readily accessible test substrates **30**, **32**, and **34**[28], were coupled to the chemically very attractive substitution pattern in the resulting dodecahedranes **31**, **33**, and **35**. The spatial situation, on the other hand, in these bisseco diones appeared somewhat unpromising insofar as the *syn*-methylene hydrogen atoms to be transferred, the H–O distances being very similar to that in **I/K**, are found at τ angles of 75–90°, that is nearly perpendicularly



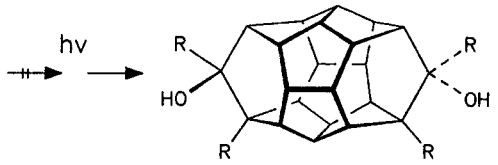
oriented with respect to the carbonyl plane (cf. the non-attacked ε-hydrogen atoms in **I**/**K**). There was some hope, though, that the triplet π,π*-excited state[29] would be adequate for the job. In the event, under all irradiation conditons tried (150-W, 450-W, 2000-W Hg high-pressure lamp; Durane filter; isooctane, tetrahydrofuran, acetonitrile; addition of *tert*-butyl alcohol to enhance diradical lifetime[30], 1–5 h), no structural change at all could be accomplished by using light of wavelengths >280 nm, a result not uncommon for rigid, non-acitvated polycyclic ketones[31]. Light of shorter wavelength (>220 nm, Vycor filter) induced slow transformation resulting in olefinic, non-identified material (oligomers).

Since it is known that the stereoelectronic requirements for hydrogen abstraction in the homo-Norrish-type II reaction are less pronounced in the solid state (O–H distances as long as 3.10 Å, τ angles up to 65° are tolerated)[27], the three test diones were also irradiated in the solid state as thin layers; again there was no obervable net change within 5 h of irradiation time.

As a further comment on the limitations of the homo-Norrish-type II procedure and as an introduction to the eventual breakthrough in our synthetic endeavor, we cite here findings with the *syn,syn*-diacylbissecododecahedranes **36a**, **b**. No ε-hydrogen transfer[32] with subsequent cyclization to the bishomododecahedranes **37a**, **b** could be effected, even though the stereochemical situation seemed rather promising. From the irradiation of the dibenzoyl derivative **36b** in tetrahydrofuran only a minor quantity (ca. 20%) of **36c**, resulting from hydrogen abstraction from the solvent[33] and radical recombination, was produced.



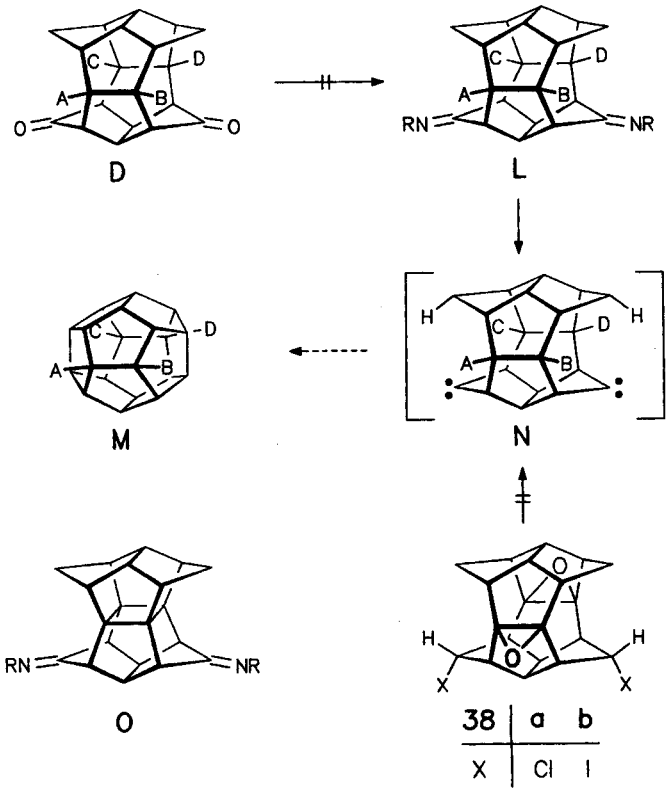
36	a	b	c
R	CH_3	C_6H_5	C_6H_4–THF



37

With a calculated exothermicity of −9.4 (−22.4) kcal/mol for the isomerization of diones **30** (**34**) to diols **31** (**35**), the base-promoted homoketoenolization involving the opposite δ-hydrogens seemed not totally out of reach. Such isomerizations had been described for other cage ketones[34] under classical keto → enol isomerization conditions (*tert*-butyl alcohol/*t*BuOK, 250°C). The diones **32** and **34** reacted very slowly (total conversion after 10–12 h) by using the same base system at 300°C, and in both cases only benzenoid products could be discovered by ^{1}H-NMR analysis. When speculating about a course for such complex degradations, one is reminded of the thermal disruption of the C_{20} pagodane skeleton into two C_{10} halves[35].

In the bisseco biscarbenes **N** a 1,2-insertion is Bredt-prohibited, whilst a transannular 1,5-insertion into the opposite *syn*-CH-bonds and thus the formation of dodecahedranes **M** should be stereoelectronically favorable[36]. Unfortunately, various bisseco diones **D** (e.g. **30**, **32**, **34**), could not be converted into bisoximes or bishydrazones (**L**), irrespective of the kind of substitution (hybridization) of the central carbons, even under very forcing reaction conditions. This behavior is not uncommon for congested cage ketones[37]. Prohibitive steric congestion for the potential tetragonal intermediates in the lateral half-cages has earlier been invoked to explain the inertness of the carbonyl function on the open side of secopagodanediones[1,2]. The correspondingly derivatized pagodanes **O** cannot be utilized as alternative precursors of dicarbenes **N** as these functional groups do not survive the opening of the four-membered ring. Attempts to arrive at biscarbenes of type **N** by α-elimination in appropriate dihalogenides (e.g. *anti,anti*-dichloride **38a** or *anti,anti*-diiodide **38b**) were unsuccessful, partly due to complications introduced by the epoxide rings[28]. Further activities along this carbene track were likewise abandoned when simultaneously explored alternative routes proved highly expeditious.



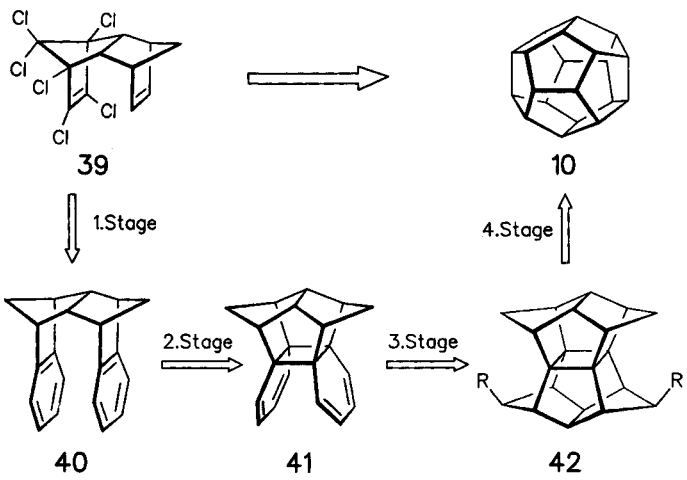
38	a	b
X	Cl	I

Summary and Outlook

Our efforts to complete the stepwise pagodane → dodecahedrane route by dehydrogenative ring closure in the saturated (bis)seco intermediates, the fourth stage in our original tactical scheme[2], have been rewarded. Yields up to ca. 53% of (methyl)dodecahedranes were an exhilarating achievement at the time, clearly better than in our shorter

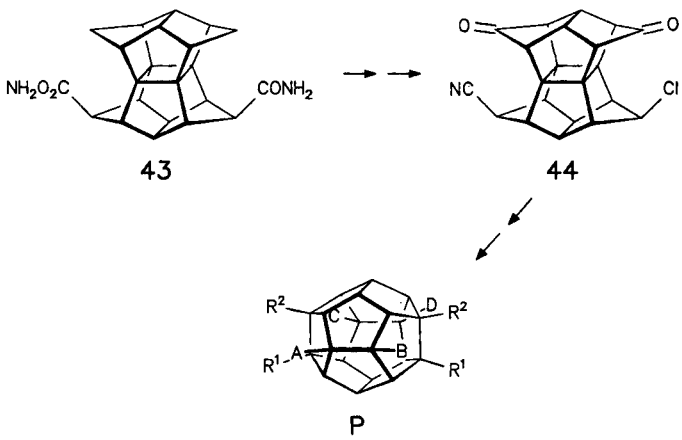
catalyzed route A and truly comparable to the results reported for the Paquette synthesis[4]. The excitement was only slightly damped by the fact that the (methyl)dodecahedranes show up as mixtures of varying composition. After all, a true "tour de force" – full of unexpected and frequently road blocking events – had been brought to a happy end. To allow a quick recapitulation of this tour in its full length, all four stages are abstracted in Scheme 4. Isodrin (**39**), the starting material (also in Woodward's first synthesis of the triquinacene half of **10**[38]), used to be a cheap technical product but nowadays is marketed as a fine chemical. The first three stages have already been critically evaluated[10]: The twofold benzoannulation sequence **39** → **40**, the [6 + 6] photocycloaddition in the unusually proximate "face-to-face" dibenzo structure **40** (→**41**), and the multistep conversion of the kinetically sufficiently stable *syn,syn-o,o'*-dibenzene **41** into the pagodanes **42**.

Scheme 4



Historically, it was the discovery of the novel benzo,benzo photocycloaddition reaction[39] which had triggered the entire project. Though an early intermediate (between **39** and **40**) has been prepared on the kg-scale and though most manipulations have been made amenable to rather large-scale and high-yield preparations, the amount of labor necessary for the production of multigram amounts of pagodanes **42** admittedly restricts their availability somewhat. For this reason and more so under the aspect of preparative exploitation of the final dodecahedranes, the outcome of the fourth stage as presented in this pager ("first-generation dodecahedranes") cannot truly satisfy. With the Paquette approach, the catalytic and the stepwise realization of this last stage (routes A and B) share the kind of complications and limitations that are inherent in the energetically highly demanding dehydrocyclization methodology. In addition, the special geometrical and energetic properties of the bisseco intermediates, which are responsible inter alia for the strict hyperstability of the bisseco enes[2] and for the propensity of the saturated bisseco compounds for 1,2-hydrogen elimination, complicate the situation by strongly promoting transannular bond formation.

The first attempts to circumvent the dehydrocyclization methodology by application of alternative, photochemical or carbenoid, ring closure procedures to bisseco intermediates, derived from 4,9-disubstituted pagodanes, turned into an exercise in futility. There was indeed little comfort in the notion that these failures have precedents and that there are reasonable explanations[40]. The obvious way out of this dilemma, the installation of functionalities into all four methylene positions of the pagodane/bissecododecahedrane skeletons that would allow the use of more tolerant techniques for the creation of the last two bonds, was therefore an early defined variation in our general isodrin → pagodane → dodecahedrane concept. In the end, it was in the pagodane-*syn,syn*-dicarboxyamide **43** that with the help of a Barton variant the two non-activated methylene groups could be functionalized. After a fascinating, truly cage-promoted multistep but one-pot reaction sequence, including intramolecular oxygen transfer, the diketo dinitrile **44** could be acquired in nearly quantitative yield[18]. With such 4,9,14,19-tetrafunctionalized pagodanes as now conveniently accessible entries into route B, and with the straightforward installation of the ultimate C,C bonds by aldol-type addition[18,41] or S_N2-substitution methodologies[19,20], a multitude of dodecahedranes containing up to eight functionalities (**P**) or even highly bent C=C bonds on their molecular suface is rapidly emerging. This "second-generation" harvest includes practically all those substituted dodecahedranes (**18**, **19**, **27**–**29**, **31**, **33**, **35**), that have escaped our assaults delineated in this paper. It is also along this pathway, implying an optimized protocol for the double decarboxylation in dicarboxylic acid **27b**[42], that parent dodecahedrane **10** is now prepared in quantities large enough for e.g. combustion experiments[43]. Undoubtedly, the prospects for the isodrin → pagodane → dodecahedrane project, if somewhat blurred by the present study focusing on the dehydrocyclization stratagem, are brighter than ever. In addition, it is by variations of the original synthetic scheme, that access is provided to numerous novel homo- and heteropolycyclic compounds of appealing structural intricacy.



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acknowledged. B. A. R. C. M. and P. R. S. thank the *Alexander-von-Humboldt-Stiftung* for post-doctoral fellowships.

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. – UV: Perkin-Elmer Lambda 15. – ^{1}H NMR: Bruker WM 250, WM 400; if not specified differently the 250-MHz data are given; ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts relative to TMS (δ = 0), coupling constants in Hz; assignments indicated with * can be interchanged. – MS: Finnigan MAT 44S. – Pd/C catalyst: Engelhard; **caution**: after the hydrogenation experiments, deactivation by addition of a few ml of CCl_4 is necessary. Addition of hexane or benzene to the reaction mixtures without deactivation can lead to ignition.

1,10-Dimethyl- and 1,11-Dimethylnonacyclo[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 (**2/3**): An intimate mixture of **1**[2] (100 mg, 0.35 mmol) and Pd/C (2 g, 10%) in a glass ampoule is dried by repeated alternate evacuation and flushing with N_2. The ampoule is placed in an autoclave, flushed well with H_2, then sealed at 20 atm H_2 and heated to 150°C for 6 h. The mixture is cooled to room temp., deactivated by addition of a few ml of CCl_4 and extracted with *n*-hexane in a Soxhlet extractor for 6 h. Evaporation of the solvent of the extract gives a colorless, microcrystalline powder (92 mg, 91%), which contains a ca. 2:3 mixture of **2** and **3**. By fractional crystallization from benzene/ethanol, **2** can be enriched to ca. 20:1 which allows a detailed NMR-spectroscopical characterization of both components. – **2/3** (2:3): IR (KBr): $\tilde{\nu}$ = 3040, 2992, 2847 (C–H) cm^{-1}. – MS (EI): *m/z* (%) = 292 (40) [M$^+$], 277 (100).

2: ^{1}H NMR (400 MHz, $CDCl_3$): Figure 1; (400 MHz, C_6D_6): δ = 3.35 (d, 3*s*-, 8*s*-, 13*s*-, 18*s*-H), 3.12 (m, 5-, 6-, 15-, 16-H), 2.83 (m, 4-, 7-, 12-, 19-H), 2.70 (m, 11-, 20-H), 2.40 (m, 2-, 9-, 14-, 17-H), 1.57 (dt, 3*a*-, 8*a*-, 13*a*-, 18*a*-H) 1.25 (s, CH_3); $J_{3a,3s}$ = 15; $J_{2,3a}$ = $J_{3a,4}$ = 7.5. – ^{13}C NMR ($CDCl_3$): Figure 1; (C_6D_6): δ = 65.6 (C-5, -6, -15, -16), 62.6 (C-11, -20), 60.1* (C-1, -10), 57.2 (C-2, -9, -14, -17), 47.2 (C-4, -7, -12, -19), 44.0 (CH_3), 35.4 (C-3, -8, -13, -18).

3: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (m, 3*s*-, 13*s*), 2.63 (m, 5-, 6-, 15-, 16-H), 2.17 (m, 7-, 9-, 17-, 19-H), 1.94 (2-, 4-, 12-, 14-H), 1.83 (m, 8*s*-, 18*s*-H), 1.37 (m, 8*a*-, 18*a*-H), $\approx$ 1.3 (3*a*-, 13*a*-H), 1.02 (CH_3); (400 MHz, C_6D_6): δ = 3.50 (d, 3*s*-, 13*s*-H)*, 3.23 (d, 8*s*-, 18*s*-H)*, 3.12 (m, 5-, 6-, 15-, 16-H), 2.83 (m, 7-, 9-, 17-, 19-H), 2.72 (m, 10-, 20-H), 2.40 (m, 2-, 4-, 12-, 14-H), 1.50 (3*a*-, 13*a*-H)**, 1.48 (m, 8*a*-, 18*a*-H)**, 1.26 (s, CH_3); $J_{2,3a}$ = 7; $J_{3a,3s}$ = 14.5; $J_{3a,4}$ = 7; $J_{4,11}$ = 13.5; $J_{6,2}$ = $J_{6,7}$ = 8. – ^{13}C NMR ($CDCl_3$): δ = 65.6 (C-5, -6, -15, -16), 62.9 (C-10, -20)*, 60.4 (C-1, -11)*, 57.8 (C-2, -4, -12, -14), 46.6 (C-7, -9, -17, -19), 43.7 (CH_3), 35.6 (C-3, -13)*, 35.0 (C-8, -18)*.

Hydrogenolysis of **4**: Carefully dried and degassed intimate mixtures of **4** (40 mg) and Pd/C (4 g, 10%) were heated at 50 atm H_2. After thorough extraction (soxhlet, 3 h), the solid residue (80–90%) is analyzed by GC/MS and ^{1}H NMR ($CDCl_3$):

T [°C]	*t* [h]	**5**	**6**	**7**	Others
80	22	20%	41%	31%	8%
100	1.5	73	10	10	7
100	6	15	60	20	5

5: ^{1}H NMR ($CDCl_3$): δ = 3.38 (d, *J* = 15), 3.27 (d, *J* = 15), 1.21 (s), etc. – MS *m/z* (%) = 278 (16) [M$^+$], 263 (100) [M$^+$ – CH_3].

6: ^{1}H NMR ($CDCl_3$): δ = 3.15 (d, *J* = 13.5), 3.03 (d, *J* = 13.5), 1.19 (s), etc. – MS: *m/z* (%) = 276 (30) [M$^+$], 261 (100) [M$^+$ – CH_3].

7: ^{1}H NMR ($CDCl_3$): δ = 2.75 (d, *J* = 13.5), 0.95 (s), etc. – MS: *m/z* (%) = 276 (4) [M$^+$], 261 (100) [M$^+$ – CH_3].

2-Methyldecacyclo[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 (**7**): A ^{1}H-NMR tube with a sample of **4** (55 mg, 0.2 mmol) is flushed with N_2, capped and heated to 300°C for 3 h to give **7** quantitatively. **7** is also formed quantitatively when a mixture of **4** and Pd/C (tenfold) is heated at 260–270°C for 30 min. Colorless crystals, no m.p. up to 340°C, slow sublimation above 180°C, light brown discoloration above 300°C. – IR (KBr): $\tilde{\nu}$ = 3000, 2960, 2920, 2860, 2840 (C–H) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): Figure 1, δ = 0.98 (s, CH_3). – ^{13}C NMR ($CDCl_3$): Figure 1; C-1, -2, -11 signals are not observed. – MS (EI): *m/z* (%) = 276 (10) [M$^+$], 261 (100) [M$^+$ – CH_3].

Methyldodecahedrane (Methylundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane) (**9**) *and Dodecahedrane* (**10**)

a): An intimate mixture of **4** (55 mg, 0.2 mmol) and Pd/C (10%, 0.5 g) is placed in a glass ampoule and dried through repeated alternate evacuation and flushing with N_2. It is placed in an autoclave, flushed well with H_2, sealed at 50 atm H_2, and heated to 100°C over a period of 3 h. After cooling to room temp., the H_2 pressure is reduced to 5 atm, and the ampoule is sealed and heated again to 250°C over a period of 6.5 h. The mixture is cooled to 0°C, deactivated by addition of a few ml of CCl_4 and extracted with hexane in a soxhlet extractor for 3 h. Filtration of the small amounts of catalyst followed by removal of the solvent gives ca. 50 mg of a solid residue. GC/MS analysis shows the following composition (*m/z*, retention time [min]): 2.8% of **10** (260, 34.75), 37.4% of **9** (274, 25.60), 1.4% of ?? (280, 19.86), 8% of ?? (278, 12.65), 12% of **5** (?) (278, 11.25), 24% of **7** (276, 9.37).

b): In an alternative experiment, the above mixture of **4** (55 mg, 0.2 mmol) and catalyst is heated to 250°C under 5 atm H_2 over a period of 6 h and worked up as above. A GC/MS analysis shows (*m/z*, retention time [min]): 9.4% of **10** (260, 35.43), 30.4% of **9** (274, 26.09), 3% of X (280, 20.26), 9% of Y (278, 12.91), 5% of **5** (278, 11.47), 21% of **7** (276, 9.57).

c): In another experiment, the heating period is reduced to 3 h. A GC/MS analysis shows (*m/z*, retention time [min]): 10% of **10** (260, 34.99), 30% of **9** (274, 25.72), 8% of X (278, 12.70), 3% of Y (278, 11.28), 20% of Z (276, 9.40).

Sublimation of the mixture from a) and b) (5 mg) at 80°C/ca. 1 Torr for 30 min gives a sublimate (4 mg) containing **10** (7%) and **9** (35%), and side products (GC), and leaving behind a mixture (ca. 1 mg) of **9** (20%) and **10** (80%), which can be sublimed at 140°C (ca. 1 Torr), leaving behind no residue. – **9**: ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.43, 3.35, 2.91, 1.13 (CH_3). – ^{13}C NMR ($CDCl_3$): δ = 75.6, 74.7, 66.8, 67.2, 67.1, 66.4, 32.6 (CH_3).

1,16- (**13**) *and 1,6-Dimethyldodecahedrane* (**14**)

a): The above ca. 2:3 mixture of **2** and **3** (40 mg), dried and degassed, and 10% Pd/C (4 g) are heated at 5 atm H_2 to 300°C for 6 h. After extraction and filtration over silica gel, 30–34 mg (75–83%) of a solid mixture is isolated. GC/MS analysis shows (*m/z*): 29% of **7** (276), 28% of X (290), 29% of **13** (288), 1% of **9** (274), 1% of **14** (288).

b): Pure **2** (10 mg) and 10% Pd/C (1 g) are heated at 5 atm H_2 to 310°C for 8 h. The crude material (9 mg, 90%) consists of 25% of **7**, 20% of **13**, 28% of **9**, 11% of **10**, and 7% of non-identified components. **13** and **14** are identified by their ^{1}H- and ^{13}C-NMR spectra which correspond to those of ref.[9]

Undecacyclo[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 (**15b**): A solution of **15a**[2] (50 mg, 0.12 mmol) in dry THF (50 ml) is heated with finely distributed Na (200 mg) and *tert*-butyl alcohol (2 ml) at reflux for 6 h. Excess of Na is cautiously destroyed with wet THF, and then the mixture is diluted with H_2O (200 ml) and exhaustively extracted with CH_2Cl_2. The united organic phases are washed twice with H_2O (50 ml), dried ($MgSO_4$), and concentrated in vacuo to give a colorless solid (40 mg, 97%) which is crystallized from ethanol/ether, m.p. 218–220°C. – IR (KBr): $\tilde{\nu}$ = 3020, 2980, 2918, 2874 (C–H) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (d, 3*s*-, 8*s*-, 14*s*-, 19*s*-H), 2.97 (m, 6-, 16-H), 2.74 (m, 5-, 17-H), 2.55 (dd, 2-, 7-, 15-, 20-H), 2.25 (t, 4-, 9-, 13-, 18-H), 1.51 (s, 22-, 23-, 24-, 25-H), 1.45 (m, 3*a*-, 8*a*-, 14*a*-, 19*a*-H), 0.22 (s, 11-H); $J_{2,3a}$ = 7.5, $J_{2,6}$ = 10, $J_{3a,3s}$ = 14.5, $J_{3a,4}$ = 6, $J_{4,5}$ = 6, $J_{5,6}$ = 11.0. – ^{13}C NMR ($CDCl_3$): δ = 68.4 (C-5, -17), 61.5 (C-1, -21), 60.8 (C-6, -16), 55.7 (C-2, -7, -15, -20), 50.4 (C-4, -9, -13, -18), 46. 9 (C-10, -12), 42.1 (C-22, -25), 36.2 (C-11), 35.6 (C-3, -8, -14, -19), 15.7 (C-23, -24). – MS (EI): *m/z* (%) = 331 (30) [M$^+$ + 1], 330 (100) [M$^+$], 273 (74).

10-Methyldecacyclo[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}]tetracosane (**16**): An intimate mixture of **15b** (50 mg, 0.15 mmol) and Pd/C (5%, 250 mg) is heated at 50 atm H_2 in an autoclave to 150°C for 2 h. The mixture is then extracted with CH_2Cl_2, the solution filtrated over a short pad of silica gel and concentrated in vacuo to give **16** (46 mg, 93%), colorless crystals, m.p. 144–146°C (ethanol/CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3036, 2910, 2842 (C–H) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): Figure 2; $J_{4,5}$ = 9, $J_{4,11}$ = 13, $J_{5,6}$ = 12, $J_{5,9}$ = 9, $J_{8a,9}$ = 7.5. – ^{13}C NMR ($CDCl_3$): Figure 2; δ = 41.9, 41.8 (C-21, -24), 15.6, 15.5 (C-22, -23). – MS (EI): *m/z* (%) = 332 (24) [M$^+$], 276 (34), 275 (100).

1-Methyl-6,16-tetramethylenedodecahedrane (**17**): An intimate mixture of **16** (5 mg, 0.015 mmol) and Pd/C (10%, 50 mg) is heated at 2 atm H_2 to 280°C for 4 h. The mixture is then extracted with hexane to give a colorless solid (ca. 3 mg, 60%), which consists of **17** (ca. 30%), **10** (2–3%, *m/z* = 260) and several non-identified components with *m/z* between 274 and 328 according to GC/MS analysis. – **17**: MS (EI): *m/z* (%) = 329 (28), 328 (100) [M$^+$], 313 (16), 300 (15), 287 (17), 273 (32), 260 (14).

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-1,10,11,20-tetrol (**21c**): A solution of **21b**[2] (69 mg, 0.1 mmol) in CH_2Cl_2 (50 ml) is stirred in a H_2 atmosphere with a catalytic amount of Pd/C. After 0.5 h, the solution becomes opaque, and the very unsoluble **21c** begins to settle. The mixture is stirred to total conversion (TLC control, ca. 24 h), then filtrated to give **21c** (33 mg, 100%), m.p. >330°C, which is not sufficiently soluble in any solvent for a NMR-spectroscopical measurement. – IR (KBr): $\tilde{\nu}$ = 3302 (OH), 3044, 2936, 2850 (C–H) cm^{-1}.

anti-3,anti-8-Dichloro-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 (**38a**): A solution of **56** (of ref.[11]) (100 mg, 0.30 mmol) in $CHCl_3$ (10 ml) is heated with benzoylperoxycarbamic acid (220 mg, 1.2 mmol) to 40°C to total conversion (4 h, TLC control). Excess peracid is destroyed by the addition of silica gel (300 mg), and the solution is filtrated over silica gel (CH_2Cl_2) to give **38a** (105 mg, 96%) as colorless, slightly air-sensitive crystals, m.p. >310°C. – IR (KBr): $\tilde{\nu}$ = 2950 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 5.67 (s, 3*s*-, 8*s*-H), 3.70 (m, 5-, 6-H), 2.94 (m, 2-, 4-, 7-, 9-, 16-, 17-H), 2.75 (d, 14*s*-, 19*s*-H), 2.62 (m, 13-, 15-, 18-, 20-H), 1.63 (dt, 14*a*-, 19*a*-H); $J_{14a,14s}$ = 14.8. – ^{13}C NMR ($CDCl_3$): δ = 84.1 (C-1, -10, -12, -21), 65.1 (C-5, -6), 63.8 (C-3, -8), 62.2 (C-16, -17), 54.4 (C-2, -4, -7, -9), 45.3 (C-13, -15, -18, -20), 32.8 (C-14, -19). – MS (EI): *m/z* (%) = [362 (20), 360 (34)] [M$^+$], 327 (22), 325 (60).

anti-3-,anti-8-Diiodo-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 (**38b**): To a solution of **84b** (of ref.[2]) (30 mg, 0.08 mmol) in CCl_4 (30 ml), lead tetraacetate (0.5 g, 1.12 mmol) and I_2 (160 mg, 1.26 mmol) are added, and the mixture is heated at reflux for 1 h while being irradiated with a daylight lamp (300 W; Osram Ultra-Vitalux). The violet solution is filtrated, washed with aqueous Na_2SO_3 solution, filtrated over silica gel and concentrated in vacuo to give **38b** (17 mg, 38%), colorless crystals, m.p. 262–268°C. – IR (KBr): $\tilde{\nu}$ = 2935 (C–H) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (s, 3*s*-, 8*s*-H), 3.97 (m, 5-, 6-H), 3.14 (m, 2-, 4-, 7-, 9-H), 2.88 (m, 16-, 17-H), 2.85 (d, 14*s*-, 19*s*-H), 2.62 (m, 13-, 15-, 18-, 20-H), 1.60 (dt, 14*a*-, 19*a*-H); $J_{14a,14s}$ = 14.5 Hz. – ^{13}C NMR ($CDCl_3$): δ = 83.3 (C-1, -10, -12, -21), 64.9 (C-16, -17), 64.7 (C-5, -6), 56.6 (C-2, -4, -7, -9), 45.3 (C-13, -15, -18, -20), 32.4 (C-14, -19), 31.3 (C-3, -8). – MS (CI, CH_4): *m/z* (%) = 545 (10) [M$^+$ + 1], 417 (100), 291 (49).

☆ Dedicated to Prof. Dr. *George A. Olah* on the occasion of his 65th birthday.

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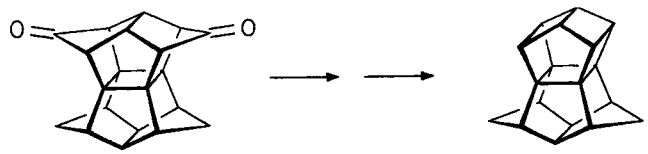

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