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From Pagodanes to Dodecahedranes - Search for a Serviceable Access to the Parent ($C_{20}H_{20}$) Hydrocarbon**

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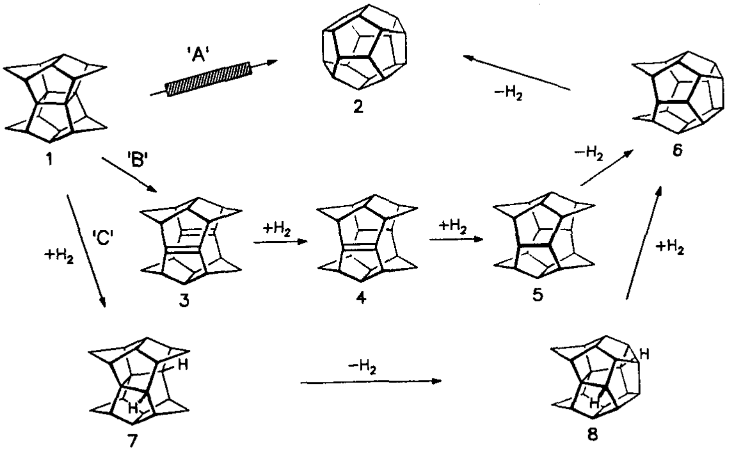
Abstract: By taking advantage of the novel S_N2 pagodane → dodecahedrane routes a preparatively potent access to the parent pentagonal dodecahedrane (**2**) was explored. The one-pot catalytic procedure ($Pd/C/H_2$) starting from an eightfold functionalized secopagodane (**14**, $C_{20}H_{12}Br_6$ $(CO_2\ CH_3)_2$) excells in shortness but, rather erratic (33-53%), falls out of the competition. The longer route via 1,6-dicarboxyl/dibromo dodecahedranes (**35**, **22**) turned out as first choice with a total yield of 74-76% based on the common pagodane precursor (**13**).

Introduction - Prior work

The parent pentagonal dodecahedrane **2** was a widely sought target in organic synthesis.[1] Subsequent to the first success by the Paquette group[2] our pagodane-dodecahedrane scheme[3] developed into a powerful synthetic alternative (aldol-, S_N2-approaches[4]). Dodecahedrane **2** enjoys renewed prominence being perhydro C_{20} fullerene.[5,6] In this paper we detail our activities directed toward a serviceable synthesis of **2** which were origi-



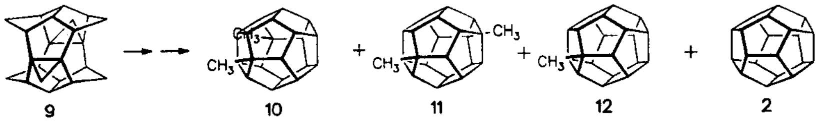
Scheme 1

**Dedicated to Professor *W. von E. Doering* on the occasion of his 80th birthday. H. P. very fondly remembers his two post-doc years at Yale University (1957-59).

nally based on the S_N2 pagodane → dodecahedrane route[3] and were more recently decisively furthered by major improvements of this approach (S_N2-New(1) and (2)).[7]

Our first try at **2** (Scheme 1, Route 'A'), the Lewis-acid catalyzed isomerization of pagodane **1**, is highly favorable in energy terms[8] and, performed as a collaborative effort with P. von R. Schleyer and W. F. Maier[9], was successful, yet disappointing in that the yields were not better than 8%. Even worse, separation of **2** from a plethora of additional products (mainly **7**, "dead end") meant significant loss. The parallel attempts with G. A. Olah and G. K. S. Prakash to effect the transformation **1** → **2** with the help of super-acids ended with a complete failure - the discovery of bis-σ-homoaromatic 4c/2e dications providing some comfort.[10]

Major hurdles in the two pathways subsequently conceptualized for stepwise isomerization **1** → **2** - abstracted with the hydrogenative/dehydrogenative sequences 'B' and 'C' in Scheme 1 - are the hyperstability of monoene **4** and above all the extreme kinetic stability of the secoskeleton **7**.[11] In fact, when side tracks such as the conversion of **3** (**4**) to **7** were restricted by structural modifications as e.g. in **9**, the total yield of dodecahedranes **2** and **10-12** increased to 35%. However, when the methyl groups of **10-12** could not be neatly removed to give **2**, and separation was very inefficient, these pathways too were out of competition.[12]



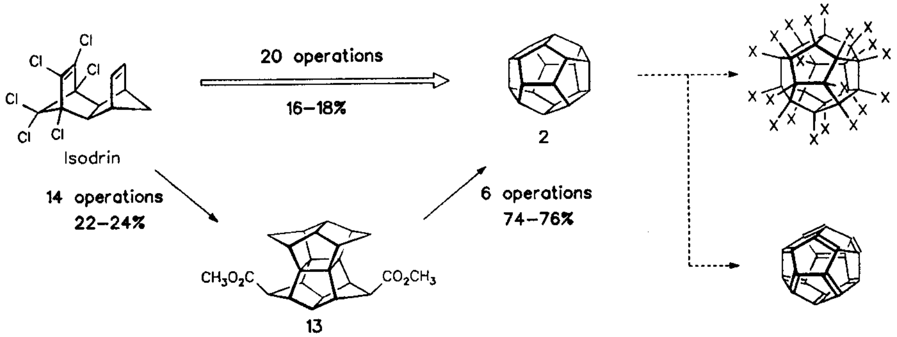
Utilization of the S_N2 Pagodane → Dodecahedrane Routes

Starting from "S_N2-intermediates"

The three versions of the S_N2-route from 4-*syn*,9-*syn*-pagodane-diester **13** - a direct offspring of the pagodane synthesis[13] - to functionalized dodecahedranes made the variously brominated diesters **14** - **17** (derivatives of **7**, **8** ('B') and **3** ('A') in Scheme 1) available in preparative (g) quantities.[4,7] There was therefore enough impetus to check their potential as precursors of **2** under the conditions of a short one-pot hydrogenative/debrominative procedure in spite of the potential limitations stated above.[14] After all, restrictions in total yield could potentially be compensated by procedural economy (Scheme 2). Except **15**, these substrates are functionalized in the four lateral positions to be connected what should allow a multistep tranformation into **2** through hydrogenolysis of C-CO_2CH_3/C-Br/C-OCH_3 bonds, lateral cyclization, fragmenting bromine elimination, and hydrogenation. After practicing with diesters (diacids) **13**, **23**, **33-35**, and dibromide **22**,[15] and using broad variation of catalyst, catalyst support, of their ratio, of the catalysts conditioning (dehydration, deoxygenation, dispersion), of hydrogen pressure, temperature and reaction time,[9] the standard protocol detailed in the experimental section (30 mg samples) was generally applied. In particular, very rapid heating up to ca. 350 °C - with the consequence of skeletal C-C bond ruptures and CO_2R → CH_3 reductions - was found to be essential in order to minimize reduction to secopagodane **7**. The latter purpose was also served by blowing out the evolving HBr by a gentle stream of hydrogen. The yields of **2** were low for **15** (12%, > 50% **7**), **16** (14%, > 50% **6**) and **17** (5%, > 50% **7**) but remarkably higher (33-53%) for **14**. ^{1}H NMR and GC/MS analyses for a run with total consumption of **14** demonstrated the complexity of the reaction course and are

Facit

The route from pagodane-diester **13** via its hexabromo derivative **14** (S_N2-New(1)[7]) into parent dodecahedrane **2** excells by its shortness but cannot meet the preparative standard. With the S_N2-New(2) route from **13** to dodecahedrane-diester **23** and the Barton degradation (**23**→)**35** → **22** → **2** the goal is now reached starting from **13** in six highly optimized, expeditious operations (**13** → **33** → **34** → **23** → **35** → **22** → **2**), with a total yield of 74-76% on the 500 mg - 1 g scale. The working time is now measured in weeks. Dodecahedrane for everybody? This question has been answered before:[7] The route from isodrin to **13** consisting of 14 operations (22-24% total yield) remains long and strenuous. Still, for us, with kg quantities of an early intermediate (**11** in Scheme II, lit.[13]) in stock, with the logistic and technical potential to master the total sequence within 2-3 months, the enthusiasm was strengthened for the projects which start out from **2** such as the generation of $C_{20}X_{20}$ "balls" (X = OH, F, Cl, Br) or of the missing, highly controversial,[36] smallest fullerene C_{20}.[5,37]



Acknowledgement

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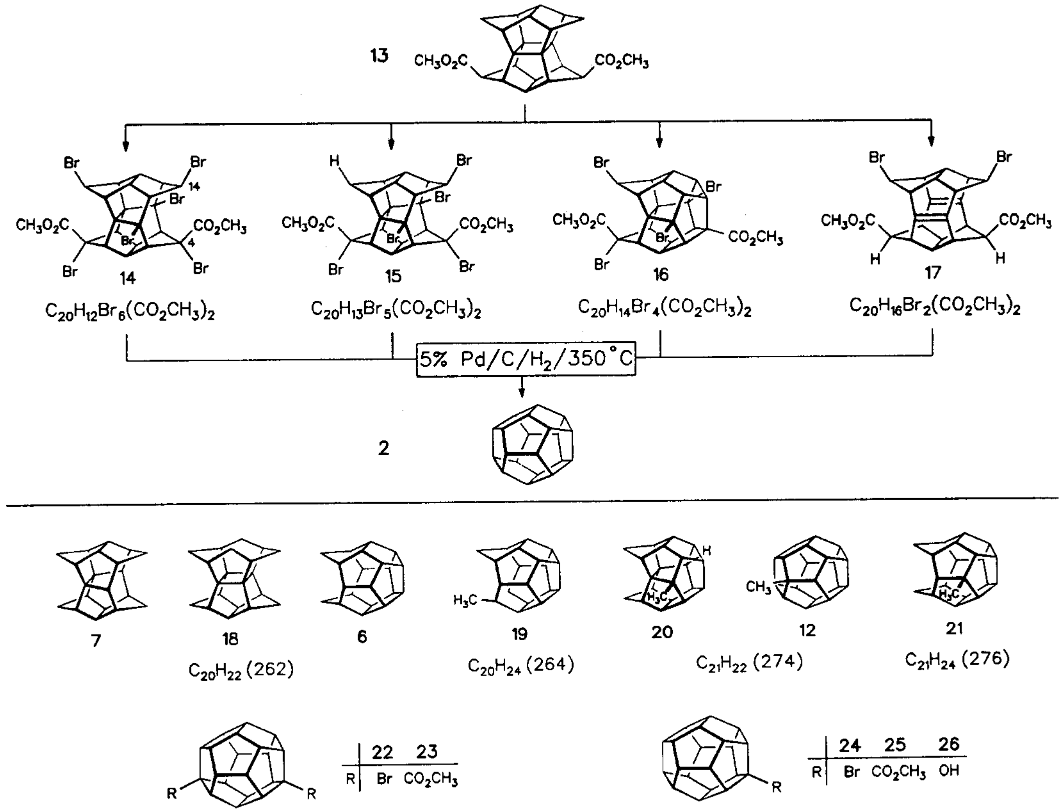
Experimental

Experimental data were recorded using the following: Melting points (mp), Bock Monoscop M; analytical TLC, Merck silica gel plates with F_{254} indicator; IR, Perkin-Elmer 457 and Philips PU 9706; UV, Perkin-Elmer Lambda 15; ^{1}H NMR, Bruker WM 250, AM 400 (if not specified otherwise, the 400 MHz spectra are given); ^{13}C NMR, AM 400, (100.6 MHz); MS, Finnigan MAT 312 (70 eV). Chemical shifts were recorded relative to TMS ($\delta = 0$), and coupling constants are in Hertz. For signal assignment, standard techniques such as homo- and hetereonuclear decoupling experiments or 2D FT COSY or heterocorrelation 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. GC/MS/DS: Var3400/TSQ7000/MSS; Ion

reproduced in Figure 1. Eight (of ca. 15) side products with *m*/*z* = 262-276 have been unequivocally identified (known hydrocarbons 7, 12, 18, carbinol 26) or tentatively assigned (20, 21) by their MS fragmentation pat-



Scheme 2

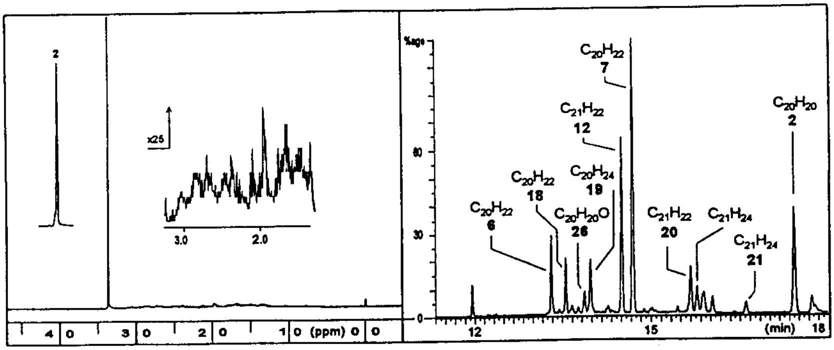
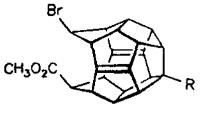


Figure 1. ^{1}H NMR (left, $CDCl_3$, 400 MHz) and GC/MS (right) analyses of a crude product mixture obtained from **14**

terns. In runs not taken to complete conversion, differing amounts of bromides **22**/**24**, of monoesters (of **6**, **7** and **2** (**25**)), and of diester **23** could also be observed. It should be realized that loss of ester groups from the sterically highly congested lateral pockets is assisted by substantial gain in strain energy.[16] A reasonable proposal as to how the eight functionalities of **14** are lost and the eight hydrogen atoms are installed en route to **2** - supported by the behavior of the other three substrates and our limited knowledge about intermediates - begins with attack at the geminally functionalized carbon of the "open" lateral side (C4) and cyclization by either radical substitution, or carbene insertion into the opposite C-Br bond (C14). This step is followed by 1,4-bromine elimination (**27**), hydrogenation (**28**), and again lateral cyclization. Note that this sequence is established for the S_N2-New(2) version.[7] Transannular C-C bond formations by radical substitution/recombination have repeatedly been deduced from MS fragmentation patterns, and seco(di)enes like **27**/**28** are, in contrast to parent bisseco(di)enes **3**/**4**, not hyperstable and are therefore less prone to transannular bond formations (cf. **4** → **7**, if at all **29**, not **30**, MM2). Once again, separation of **2** on a preparative scale from the chemically and structurally very similar admixtures became a problem. Fractional crystallization only furnished highly enriched samples of the least soluble **2**. Treatment of the crude product mixture with bromine - with quantitative transformation of **2** into its monobromide **24**[17] - was no way out of the dilemma, as partial bromination of other components again prohibited an economical separation.



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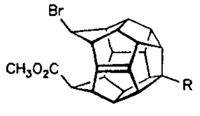

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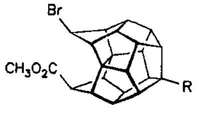

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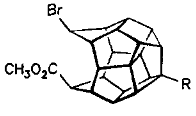

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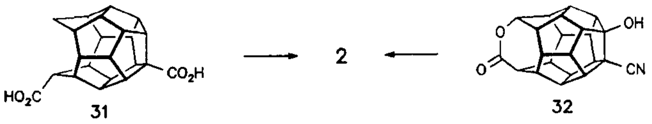
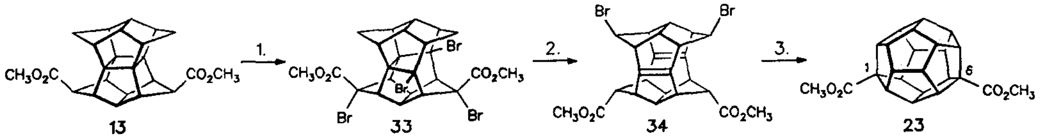
For completeness it should be added that the secododecahedrane-diacid **31**, a derivative of **6**, and the homododecahedrane **32** under the conditions applied to **13** and **23** yielded 30-40% of **2** (not optimized), submersed in the usual complex product mixtures.

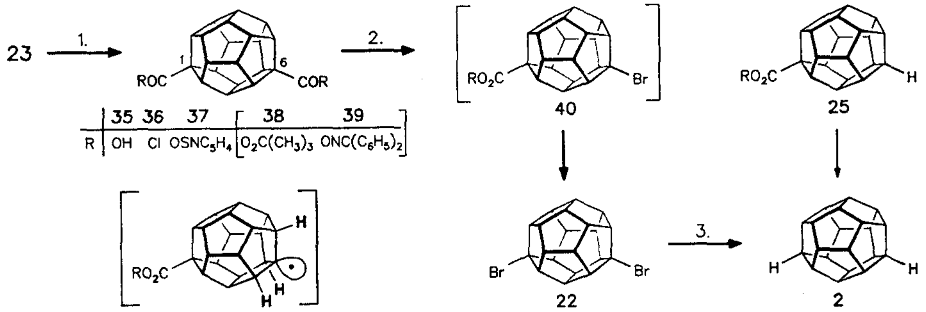


To summarize this section: With the functionalization pattern present in the hexabromodiester **14** the "dead end" marked by the secopagodane **7** in the original route 'B' (Scheme 1) can be efficiently overcome. With two operations leading expeditiously from **13** to **14** (S_N2-New(1), 86-90%[7]) this route is indeed impressively short. Yet, with yields of 33-53% - though remarkable given the number and nature of bond-forming and bond-breaking events involved (better than 90% for every single one) - and given the restriction in sample size and analytical deficiencies, this approach was not useful for preparative work.

Starting from 1,6-difunctionalized dodecahedranes

Generation of the parent skeleton **2** starting from its 1,6-diester **23** was an alternative since the S_N2 route had paved the way (pagodane-diester **13** → **23**, nine operations, 55-65%).[4,5] This approach - popular in the area of polycycles (pagodanes,[13] adamantanes,[19] cubanes,[20] pentaprismanes[21]) - became most attractive when the recent break-through reduced the route to **23** to mere three operations and raised the total yield to 85-91%.[7] The somewhat modified, now routinely utilized S_N2-New(2) protocol **13** → **33** → **34** → **23** is detailed in the Experimental Section. Thus, enough material was at hand to extensively study the degradation **23** → **2** (Scheme 3). Of the five methods originally considered - (i) catalytic hydrodecarboxylation of diacid **35**, (ii) *in situ* thermolysis of bis-*N*-hydroxy-pyridinethione ester **37**,[22] (iii) iododecarboxylation of **35**,[13] (iv) thermolysis of bis-perester **38**,[23] and (v) photolysis of bis-oxime ester **39**[24] - the latter three were given up at early stages. It was understood a priori that methods relying on the efficient interception of dodecahedral radicals might face problems in that the parent $C_{20}H_{19}$ radical has so far withstood all attempts for its direct characterization[25] and that the three β-positioned hydrogens provide a good degree of steric protection for the radical centers.[5]





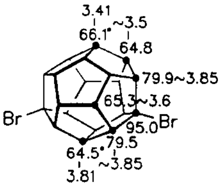
Scheme 3

(i). As the shortest procedure catalytic hydrodecarboxylation of the two non-activated tertiary carboxyl groups of **35** (quantitatively prepared from diester **23**) has been scrutinized under many of the conditions detailed above for **14** - in the EI-MS spectrum the ease of CO_2 elimination is manifested by $m/z = 302$ (100%), 257 (44%). The best results, with up to 65% of **2**, were achieved when a finely dispersed 1:10 mixture of **35** and 5% Pt/Al_2O_3 was kept at 350 °C for 10 h under a slight H_2 pressure. The sublimed material had a purity of better than 98% - the GC/MS analysis revealing **12** ($m/z = 284$) and **19** ($m/z = 264$) as impurities. Yet, problems with the reproducibility of yield and purity could not be solved to our satisfaction.

(ii). For the Barton degradation of **35** via **37** with interception of the dodecahedryl radicals by hydrogen atoms (*tert*-butyl mercaptan) as obvious first choice, the yield of **2** under modified conditions - with and without irradiation, sonification, and in line with experience gathered for functionalized analogs[6,26] - could not be raised above 40%. This procedure was therefore given up. A highly expeditious protocol for the longer alternative, bromodecarboxylation **37** → **22** followed by reduction **22** → **2** was worked out, with careful exclusion of moisture, oxygen and light, and carefully dried reagents (500 mg - 1 g scale). To this end bis-acid chloride **36** - freshly prepared by reacting a suspension of diacid **35** in benzene with oxalyl chloride and carefully freed from the reagent - was treated as a homogenous solution in $CBrCl_3$ (solubility ca. 6 mg/mL) with the *N*-hydroxypyridine-2-thione sodium salt, the solution refluxed until the yellowish coloration had disappeared. After a simple work-up procedure, yields of up to 90% of pure, high-melting dibromide **22** (mp 266 °C) were obtained. After treatment of the insoluble residue with CH_2N_2, diester **22** and bromoester **40** could be identified as the main parts of the missing material. It should be added, that the Hunsdiecker degradation[27] **35** → **22** with either the Hg,[28] Pb[29] or Ag salts[30] had provided only modest yields of at best 30%. Solubility and substitution of dodecahedranes by bromine were just two of the more trivial complications. The reduction of dibromide **22** was previously carried out by irradiation (254 nm) in the presence of TTMS (Tris-(trimethylsilyl)silane)[31] with nearly quantitative yields; it had to be learnt, however, that reproducibility in larger scales again was not satisfactory. As a reliable alternative, the reduction is now performed with Li/*tert*-butyl alcohol and is nearly quantitative and more convenient.[32]

For dibromide **22** (C_{2v}) and bromoester **40** (C_s) ^1H, ^{13}C NMR and MS data are presented in Figure 2 as confirmation of their structure. Reference data for 1,6-disubstituted dodecahedranes are found in the literature.[4,26]

m/z = i.a.
[419–415(15–17), M$^+$]
339–337(100), 259(7),
258(18), 257(30)



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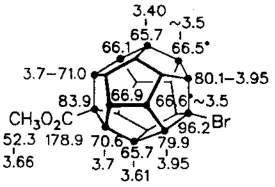

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m/z = i.a.
[399–396(0.2–2), M$^+$]
317(56), 259(20),
258(54), 257(100)

Figure 2. ^1H, ^{13}C NMR assignments ($CDCl_3$, 400 MHz) and selected MS (EI) fragments for **22** and **40**

Since for the Paquette/Gallucci structure determination of **2** only a twinned crystal had been available,[33] the analysis was repeated with a single-crystal obtained by chance from a benzene reaction solution (Figure 3).[34] From the structural data in Table 1 it can be deduced that there is a marginally better agreement with the MM3 values of Allinger for gaseous **2** (I_h).[35] The structural details, T_h symmetry and asymmetric unit containing two carbon and two hydrogen atoms, are in perfect agreement with the impressive original analysis.

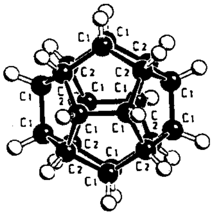

Figure 3. X-ray structure of **2**

Table 1. Comparison of Selected Calculated (MM3) and Experimental Structural Data (Å, °) of **2**

	C1-C2	C1-C1	C2-C1-C1	C1-C2-C1	C2-C1-C2	d(max)
MM3 (35)	1.545	1.545	108.0	108.0	108.0	4.331
Exp.	1.5452(12)	1.544(4)	107.97(7)	108.14(9)	107.79(13)	4.333(3)
Exp. (33)	1.541(2)	1.535(5)	107.9(4)	107.7(2)	108.1(1)	4.317(5)

Source: EI/CI[210°]; EI: 70 eV, 0.4 mA; CI: 170 eV, 0.45 mA; Column: 30 m DB5 CB [0.25 mm/0.25 µm], 2 mL He/min; Temp.[°C]: 10(2)/20/280, Inj.: 235, Coupl.: 280; Vol./Split: 0.1µL/1:20. Bromine was distilled before use. The cyclization experiments with the "P$_2$F" base^{38} were performed with best possible exclusion of air and moisture (glove box); for the yields given perfect quality of the base is essential.

Dimethyl Undecacyclo$[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$icosane-1,6-dicarboxylate (23)

(Modified version of the protocol given in lit.^{7}).

To a stirred solution of **34** (1.05 g, 2.0 mmol, prepared from **13** via **33** as described in lit.^{7}) in anhydrous benzene (100 mL) a solution of the "P$_2$F" base (6.6 g, 20.0 mmol) in anhydrous benzene (40 mL) was added. After total conversion (15 min), TLC, cyclohexane/ethyl acetate = 4:1, R_f (**34**) = 0.15, R_f (intermediate dodecahedradiene) = 0.40) anhydrous MeOH (5 mL, 123.5 mmol) and Pd/C (5%, 160 mg) were added. Hydrogen gas was bubbled through the stirred solution until no olefinic component was present anymore (5-10 min, TLC, **23** is not oxidized by $KMnO_4$). The suspension was washed with water (100 mL), the aqueous phase extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried ($MgSO_4$). The solution was concentrated *in vacuo* and filtered through silica gel (1.5/2 cm, CH_2Cl_2/ethyl acetate = 10:1, R_f (**23**) = 0.89). After evaporation the solid colorless residue consisted of pure **23** (715-722 mg, 95-96%). Elution of the silica gel with ethyl acetate (50 mL) gave the known monoester derivative of **35** (7-15 mg, 1-2%, R_f = 0.08, CH_2Cl_2/ethyl acetate = 10:1). The monoacids of several runs were combined and converted into **23** with CH_2N_2 to bring the total yield of **23** up to 96-98%.

Undecacyclo$[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$icosane-1,6-dicarboxylic Acid (35)

A suspension of **23** (1000 mg, 2.66 mmol) in methanol/water (30 mL, 5:1) and NaOH (520 mg, 9.80 mmol) was heated to reflux until the solution was homogenous (4-6 h). After concentration *in vacuo*, the residue was dissolved in water (5-10 mL) and aqueous HCl was added under cooling (0-10°C, pH < 1). The precipitate was filtered, washed with cold water (pH = 7), and dried at 120°C for 24 h. Colorless powder (921 mg, 99 %): mp > 320°C; IR (KBr) 3396 (O-H), 2934 (C-H), 1685 (C=O), 1396, 1233, 1014 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO) δ 11.95 (s, 2 COOH), 3.68 (m, 2-, 5-, 7-, 11-, 16-, 20-H), 3.52 (m, 3-, 4-H), 3.49-3.40 (m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 3.37 (m, 13-, 14-H); ^{13}C NMR ([D$_6$]DMSO) δ 179.0 (2 C=O), 83.9 (C-1, -6), 70.4 (C-11, -16), 70.2 (C-2, -5, -7, -20), 66.3 (C-8, -9, -18,-19), 66.3 (C-10, -12, -15, -17)*, 66.2 (C-3, -4, -13, -14)*; MS (EI) *m/z* (relative intensity) inter alia 348 (M$^+$, 4), 330 (33), 302 (100), 274 (12), 257 (44), 215 (6). Anal. Calcd for $C_{22}H_{20}O_4$ (348.42):C, 75.84; H, 5.79. Found: C, 75.81; H, 5.48.

1,6-Dibromo-Undecacyclo$[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$icosane (22)

The suspension of **35** (500 mg, 1.43 mmol) and oxalyl chloride (10 mL, 74.3 mmol) in dry benzene (70 mL) was heated to reflux until the mixture got homogenous (2-3 h). After concentration *in vacuo* the solid residue was freed from included oxalyl chloride by heating at 40-50 °C/10^{-2} Torr for 2 h. The colorless crystalline residue (547 mg, 100% **36**) was dissolved in dry $BrCCl_3$ (100 mL), to the degassed boiling solution under an argon countercurrent *N*-hydroxypyridine-2-thione sodium salt (700 mg, 4.67 mmol) and DMAP (10 mg) were added, the solution was heated to reflux until the yellow color had disappeared (30 min). The reaction mixture was filtered through a silica gel column (8/3 cm), the product eluted with CCl_4 (5·50 mL). After concentration *in vacuo* the colorless, crystalline residue consisted of practically pure **22** (523 mg, 89 %): mp 266°C; IR (KBr) 2940 (C-H), 1301, 1239, 845, 829, 735, 616 (C-Br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.93 (m, 2-, 5-, 7-, 11-, 16-, 20-H), 3.81 (m, 3-, 4-H), 3.63-3.58 (m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 3.41 (m, 13-, 14-H); (C_6D_6) δ 3.84 (m, 2-, 5-, 7-, 11-, 16-, 20-H), 3.48 (m, 3-, 4-H), 3.22-3.08 (m, 8-, 9-, 10-, 12-, 15-, 17-,18-, 19-H), 2.83 (m, 13-, 14-H); ^{13}C NMR ($CDCl_3$) δ 95.0 (C-1, -6), 79.9 (C-11, -16), 79.5 (C-2, -5, -7, -20), 66.1 (C-13, -14)*, 65.3 (C-8, -9, -18, -19), 64.8 (C-10, -12, -15, -17), 64.5 (C-3, -4)*; MS (EI) *m/z* (relative intensity) inter alia [419(17), 417(19, M$^+$-1), 415(15)], 339, 337(100), 259(7), 258(18), 257(30), 191(8), 179(9), 165(11), 128(16), 115(15); $C_{20}H_{18}Br_2$ (418.2).

Undecacyclo[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-1,6-dicarboxyclic Acid Dichloride (36)

Compound **36** was not isolated and only characterized by the NMR data. ^{1}H NMR (C_6D_6,) δ 3.68 (m, 2-, 5-, 7-, 11-, 16-, 20-H) 3.30 (m, 3-, 4-H), 3.17-3.04 (series of m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 2.98 (m, 13-, 14-H); ^{13}C NMR ($CDCl_3$) δ 177.8 (2 C=O), 94.3 (C-1, -6), 71.0 (C-11, -16), 70.7 (C-2, -5, -7, -20), 66.5 (C-3, -4)*, 66.4 (C-8, -9, -18, -19)**, 66.3 (C-10, -12, -15, -17)**, 66.0 (C-13, -14)*.

Methyl 6-Bromo-undecacyclo[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-1-carboxylate (40)

The reaction mixture as obtained in the protocol for **22** was poured into water and extracted with CH_2Cl_2 (5·50 mL); after concentration *in vacuo,* the residue was dissolved in MeOH/CH_2Cl_2 (1 / 1), under cooling with ice, CH_2N_2 was added until the yellow color remained. Excess CH_2N_2 was destroyed with formic acid. After concentration *in vacuo* the residue was chromatographed on silica gel (CCl_4/*n*-hexane = 2/1) to give **22** (500 mg, 85%), **40** (30 mg, 5%) and **23** (20 mg, 4%). **40**: Colorless crystals; IR (KBr) 2940 (C-H), 2840 (C-H), 1725 (C=O), 1240, 735, 620 (C-Br) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.8-4.0 (m, 5-, 7-, 16-H) 3.65-3.75 (m, 2-, 11-, 20-H), 3.66 (s, OCH_3), 3.61 (m, 3-, 4-H), 3.55-3.45 (m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 3.40 (13-, 14-H); ^{13}C NMR ($CDCl_3$) δ 178.9 (C=O), 96.2 (C-6), 83.9 (C-1), 80.1 (C-16), 79.9 (C-5, C-7), 71.0 (C-11), 70.6 (C-2, C-20)**, 66.9 (C-9, C-19), 66.6 (C-8, -18)* 66.5 (C-10, C-12)*, 66.1 (C-15, C-17)*, 65.7 (C-3, C-4)*, 65.7 (C-13, C-14)*, 52.3 (OCH_3); MS (EI) *m/z* [399(1), 398(2), 396 (2, M$^+$-1)], 317(56), 259(22), 258(52), 257(100), 165(10), 149(12), 128(17), 115(17), 84(16), 78(18). $C_{22}H_{21}BrO_2$ (397.3).

Undecacyclo[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 (2)

a) From **14**

The three-necked 50 mL flat bottomed flask with a finely powdered (agate mortar) mixture of **14** (30 mg, 0.04 mmol) and Pd/C (5%) (150 mg) was carefully deoxygenated and saturated with hydrogen by three times evacuating and refilling with N_2, then with H_2. The flask was dipped into a preheated metal bath (350°C), kept for 2 h at this temperature while leading through a soft stream of H_2. In order to minimize loss of subliming **2**, the gas was led through a cooler (20°C) from which sublimed **2** was washed off with benzene. After extraction of the black solid with benzene (75 mL, 2 h, 50°C), filtration, and concentration *in vacuo*, the crude colorless solid (8-9 mg), analyzed by GC/MS (cf. Figure 1.), was dissolved in hot benzene (ca. 2 mL). From the homogenuous clear solution 3-5 mg (33-53%) of **2** crystallized practically pure. The residue contains the complex mixture of the well soluble hydrocarbons as shown in Figure 1.

In order to confirm the yield of **2** obtained from **14**, the crude solid reaction mixture was suspended in bromine (2 mL) and stirred under exclusion of light for 24 h. After concentration *in vacuo* from the brownish crude solid residue, a complex mixture of brominated hydrocarbons, by chromatography on silica gel (20/1.5 cm, CH_2Cl_2) as the main component pure bromo-dodecahedrane **24** ($R_f = 0.62$) was isolated in yields being in line with the results of GC/MS the analyses.

Under the conditions stated for **14** the hydrogenative/debrominative procedure yielded from **15** 12%, from **16** 14%, and from **17** 5% of **2**. The GC/MS analyses revealed **7** as major product from **15** and **17** (> 50%) and **6** from **16** (> 50%).

b) From **35**

In a sublimation vessel the finely powdered mixture of **35** (100 mg, 0.29 mmol) and Pt/Al_2O_3 (5%, Aldrich) was kept for 3 h at 10^{-4} Torr, then was heated under a slight H_2 pressure (1 atm) for 8 h to 350°C. The sublimed material was analyzed by GC/MS - the 35-48 mg (47-65%) of crystalline **2** were of better than 98% purity. Two trace components were identified as **12** and **19**.

c) From **22**

To a solution of **22** (500 mg, 1.20 mmol) in *tert*-butyl alcohol (5 mL) lithium metal (167 mg, 24 mmol) was added in small portions, the mixture heated to reflux until total conversion (12 h, TLC, CCl_4/n-hexane = 2/1, $R_f(\mathbf{22}) = 0.66$; no **24** ($R_f = 0.6$, independently determined). After concentration *in vacuo* the residue was carefully extracted with aqueous NH_4Cl (5·20 mL), the remaining solid filtered and dried *in vacuo* for 24 h (P_2O_5). Sublimation at 200°C/10^{-2} Torr provided 300 mg (96 %) pure **2**: mp 430 ± 10°C; ^1H NMR (C_6D_6) δ 3.38 (s); ^{13}C NMR (C_6D_6) δ 67.0; MS (EI) *m/z* (relative intensity) inter alia 261 (23), 260 (100, M^+), 259 (24), 129 (5), 115 (5); $C_{20}H_{20}$ (260.4).[2]

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34. Crystal data for **2**: $C_{20}H_{20}$, M = 260.36, a = 10.6444(4) Å, V = 1206.05(4) Å^3, Z = 4, d_{calcd} = 1.434gcm^{-3}. crystal system: cubic, space group Fm$\bar{3}$, No. 202, crystal size [mm]: 0.2 x 0.2 x 0.2, Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, graphite monochromator, ω-2Θ-scan, collected reflections: 533, independent reflections: 183, R_{av} = 0.026, reflections observed [$I > 2\sigma(I)$]: 142, μ = 0.080 mm^{-1}, no absorption correction, solution by direct phase determination (MULTAN), full-matrix least-squares refinement on F^2 (SHELXL-93), hydrogen positions were refined isotropically, parameters 15, final indices [$I > 2\sigma(I)$]: R = 0.0414, R_w^2 = 0.1343, Goodness-of-fit : 1.188, extinction coefficient: 0.007(5), largest diff. peak: 0.252 eÅ^{-3}. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD (406032).
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