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Cross-coupling of a functionalized highly pyramidalized alkene: DSC and NMR study of the [2+2] retrocycloaddition of cyclobutane cross products, hyperstability and pyramidalization of the formed dienes

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Abstract—The synthesis, chemical trapping and ab initio calculations of the highly pyramidalized 5α,6α:11α,12α-bis(isopropylidenedioxy)pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodec-8-ene, **25**, are reported. Its cross-coupling reaction with 3,7-dimethyltricyclo[3.3.0.0^{3,7}]oct-1(5)-ene, **1b**, gave a cyclobutane derivative, **29**, which on further manipulations gave the cyclobutane derivatives **32** and **33** and the derived [2+2] retrocycloaddition dienes, **31** and **34**. Molecular Mechanics calculations show these dienes to be slightly pyramidalized but highly hyperstable. The neat conversion of **32** and **33** to **31** and **34**, respectively, has been studied by DSC, ^{1}H NMR and theoretical methods (MM2 and ab initio).

1. Introduction

Highly pyramidalized alkenes are a very interesting kind of compounds due to their unusual properties.[1–3] For instance, tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene,[4–6] **1a**, 1,2-dehydrocubane,[7] **2**, or 4,5-dehydrohomocubane,[8–9] **3**, (Fig. 1) are highly reactive towards nucleophiles and dienes while in the absence of such reagents they dimerize through a [2+2] cycloaddition reaction. Although we and others have published the synthesis, chemical trapping and dimerization of several highly pyramidalized alkenes,[10] much of the work done on this kind of alkenes has mainly been of interest to physical organic chemists,[11] owing to the lack of synthetic utility of the dimers.

Functionalized highly pyramidalized alkenes can be of much synthetic interest for the preparation of complex polycyclic compounds. Herein we report in detail[12] the first synthesis of one of such alkenes, 5α,6α:11α,12α-bis-(isopropylidenedioxy)pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]-dodec-8-ene, **25**, its trapping with 1,3-diphenylisobenzofuran and its cross-coupling with 3,7-dimethyltricyclo-[3.3.0.0^{3,7}]oct-1(5)-ene, **1b**, to give the cyclobutane derivative, **29**. Further manipulations on this compound led to other cyclobutane derivatives that were thermally transformed into functionalized tetrasecododecahedradienes. Diene **30** was converted back to their cyclobutane precursor, **29**, on irradiation. Molecular Mechanics calculations (MM2 program)[13] showed that dienes **14b**, **30**, **31** and **34** are slightly pyramidalized but highly hyperstable[14] alkenes. Conversion of the cyclobutane derivatives **32** and **33** to the corresponding dienes **31** and **34**, respectively, was studied by a combination of DSC, ^{1}H NMR and theoretical methods (MM2 and ab initio).

2. Results and discussion

The parent pyrimidalized alkene **6** was first prepared by Borden at al.[15] by reaction of diiodide **5** with *tert*-butyllithium (Scheme 1). Diiodide **5** was obtained by standard procedures from diester **4** which in turn was obtained in a one-pot reaction from dimethyl acetylenedicarboxylate and 9,10-dihydrofulvalene on a 30–40 g scale.[16] When **6** was

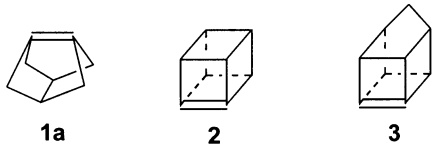

Figure 1. Structure of the highly pyramidalized alkenes: tricyclo-[3.3.0.0^{3,7}]oct-1(5)-ene (**1a**), 1,2-dehydrocubane (**2**) and 4,5-dehydrohomocubane (**3**).

Keywords: strained compounds; cycloadditions; theoretical studies; polycyclic aliphatic compounds.

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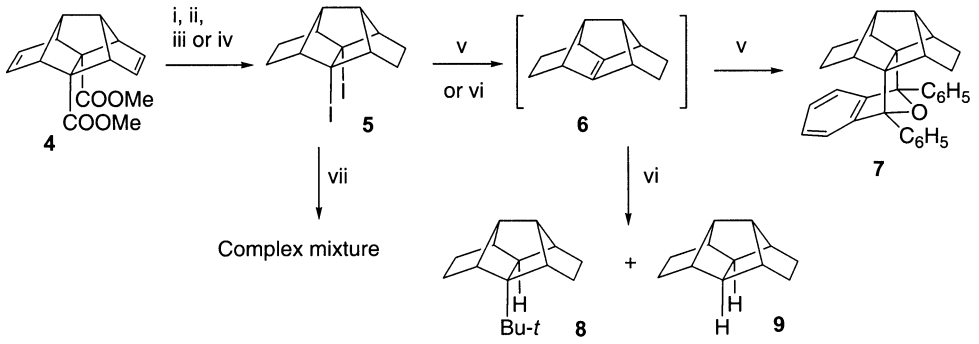
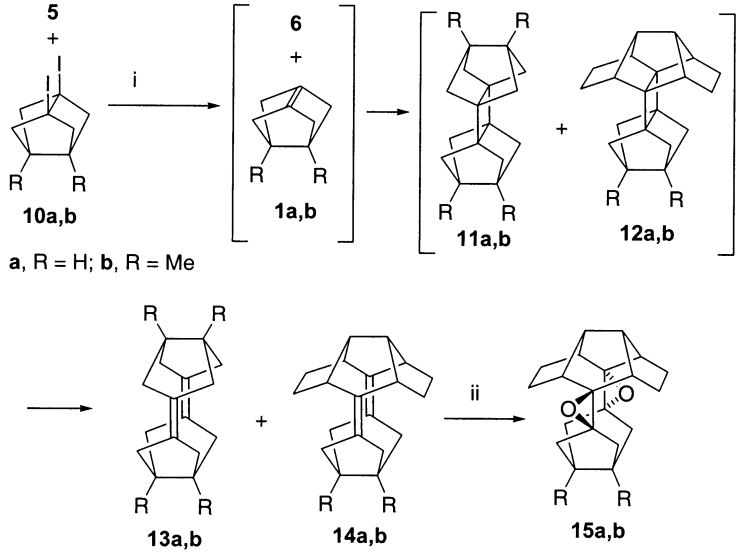


Scheme 1. Generation and reactions of pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodec-8-ene (**6**). (i) H_2, 5% Pd/C, MeOH, 1 atm, 3 h, quantitative yield; (ii) Concentrated H_2SO_4, 70°C, 30 min, 70%; (iii) Hg_2O, I_2, $h\nu$, 50% yield;[15] (iv) Iodosobenzene diacetate, I_2, benzene, $h\nu$, 4+18 h, 61% yield;[17] (v) *t*-BuLi, THF, 1,3-diphenylisobenzofuran, −78°C, 30 min, 80% yield;[15] (vi) *t*-BuLi, diethyl ether/pentane (1:1), 0°C, mixture of **8** and **9** in the ratio of 20:1; (vii) Na, 1,4-dioxane, reflux, 4 h.[17]

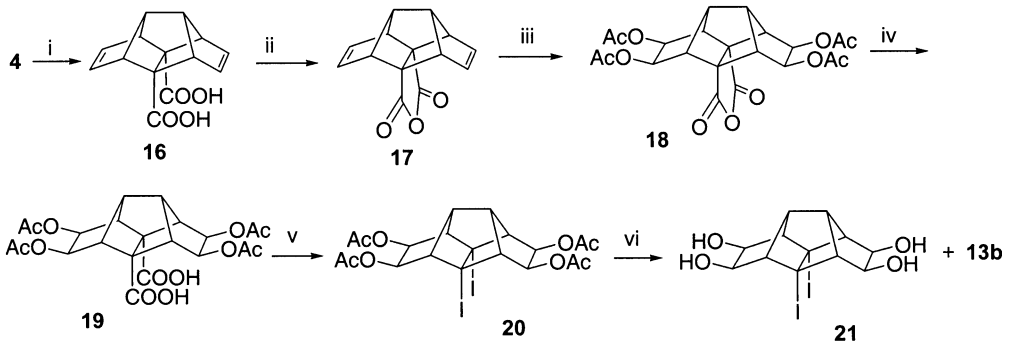
generated in the presence of 1,3-diphenylisobenzofuran, the corresponding Diels–Alder adduct, **7**, was obtained.[15] In the absence of a diene, no dimer of **6** was formed, the reduction product **9** and product **8**, derived from the addition of *tert*-butyllithium to **6**, were isolated instead. We attempted the dimerization of **6**, generated by reaction of diiodide **5** with melted sodium in boiling dioxane, but a complex mixture of products, not containing the expected dimer, was obtained.[17] Dimerization of **6** to a cyclobutane product must be very difficult due to the great steric interaction between the ethylene bridges of both halves.

Some time ago, we took advantage of the steric hindrance for the dimerization of **6** to carry out the first cross-coupling reaction of two highly pyramidalized alkenes (**6** and the unhindered **1a** and **1b**).[17] Thus, reaction of diiodides **10a** or **10b** and **5** with melted sodium afforded the tetraseco-dodecahedradienes **14a** and **14b** via the corresponding cyclobutane derivatives **12a** and **12b**. The above dienes were characterized as the corresponding diepoxides **15a** and **15b** (Scheme 2).

Later, we envisaged the synthesis of a derivative of alkene **6** functionalized at positions 5, 6, 11 and 12, taking advantage of the presence of the double bond functionality of **4** at these positions. Diiodo compound **20** was readily synthesized following the sequence shown in Scheme 3. Diacid **16**, obtained by hydrolysis of diester **4**,[16] was refluxed for 1 h with acetic anhydride to give, after sublimation, pure **17** in 86% yield. Catalytic bis-dihydroxylation of **17** using *N*-methylmorpholine-*N*-oxide (NMO) and a catalytic amount of dipotassium osmate[18] followed by treatment with acetic anhydride afforded tetraacetate **18** as a monohydrate in 87% overall yield. Subsequent basic hydrolysis afforded diacid **19** (92% yield) which was submitted to iododecarboxylation by reaction with iodosobenzene diacetate and iodine in benzene under irradiation with two 100 W tungsten lamps, following a standard protocol of the Moriarty[19] modification of the Suárez procedure.[20] After the usual work-up, diiodide **20** was obtained in only 15% yield, much of diacid **19** (64% yield) being recovered. After much experimentation, the yield of this reaction was improved to 24% by carrying out the reaction in CH_2Cl_2 as solvent and using a 60 W tungsten lamp to avoid evaporation of the solvent. Under these conditions, anhydride **18** and diacid **19** were recovered in 11 and 58% yield, respectively, (see



Scheme 2. Cross-coupling of the highly pyramidalized alkenes **6** and **1a** or **1b**. (i) Na, 1,4-dioxane, reflux, 4 h; (ii) Dimethyldioxirane, CH_2Cl_2, 0°C: **15a**, 64% overall yield, **15b**, 59% over all yield.[17]



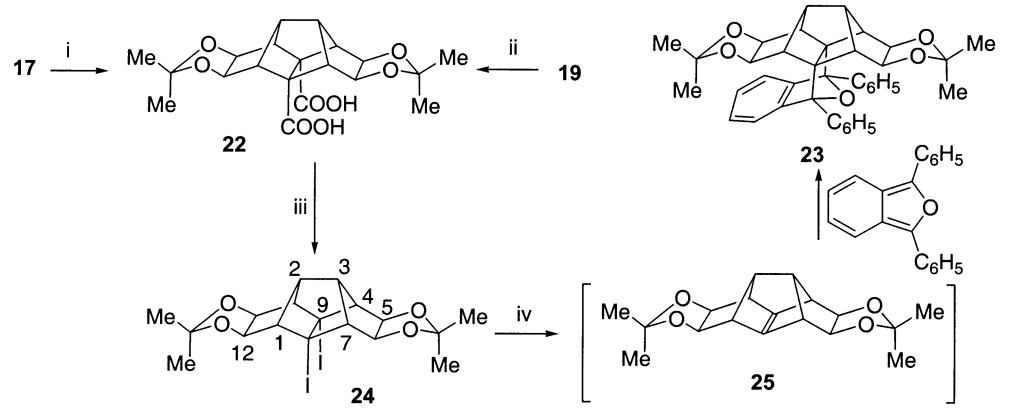
Scheme 3. Synthesis of diiodo tetraacetoxy compound **20** and attempted cross-coupling reaction with **1b**. (i) KOH, MeOH, H_2O, 0°C to room temperature;[16] (ii) Ac_2O, reflux, 1 h, 86%; (iii) (a) *N*-methylmorpholine *N*-oxide, $K_2OsO_4{\cdot}2H_2O$, *t*-BuOH/H_2O/acetone 1:1:1, (b) Ac_2O, reflux, 2 h, 87%; (iv) $NaHCO_3$, THF/H_2O, room temperature, 18 h, 92%; (v) Iodosobenzene diacetate, I_2, CH_2Cl_2, $h\nu$, 4+18 h, **20**:24%, **18**:11%, recovered **19**:58%; (vi) **10b** (3 equiv.), Na, 1,4-dioxane, reflux, 4 h, **21**:72%, **13b**:75% from **10b**.

Section 6). The isolation of anhydride **18**, a compound that cannot undergo the iododecarboxylation reaction, suggests that the low yield of the formed **20** might be due to the formation of anhydride **18** under the reaction conditions. Most of this anhydride must be hydrolyzed during the alkaline work-up, being mostly recovered as the corresponding diacid. The lower temperature of the reaction carried out in CH_2Cl_2 might reduce the formation of anhydride **18**, thus increasing the yield of **20**.

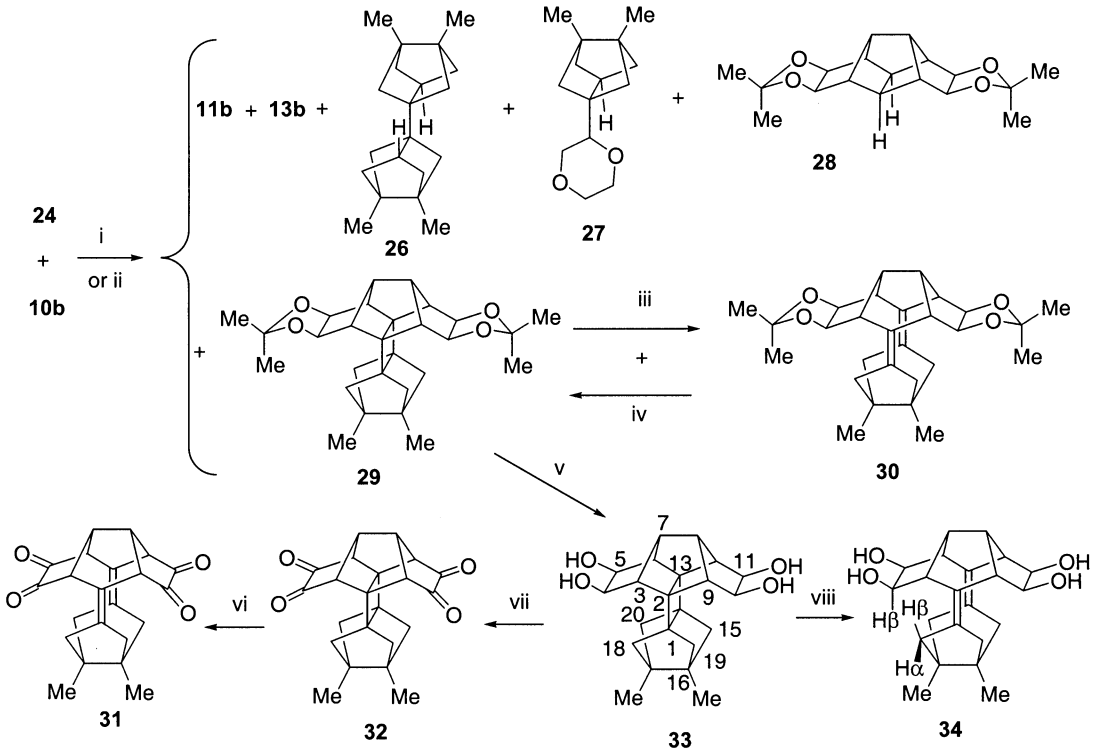
Reaction of a mixture of diiodides **10b** and **20** in the molar ratio of 1:3 with excess of melted sodium in refluxing 1,4-dioxane for 4 h gave **21** as the only isolated product derived from **20**. This fact can be ascribed to the reduction of the ester groups prior to the dehalogenation reaction. The formed sodium tetraalkoxide must be insoluble in the organic medium, thus precluding its deiodination.

To avoid the reduction of the protecting groups we decided to prepare diiodide **24**, in which the 1,2-diol functions are protected as isopropylidene acetals. Diacid **22** was easily prepared in 84% overall yield from anhydride **17**, by catalytic bis-dihydroxylation followed by acetonide formation and simultaneous anhydride hydrolysis on reaction with acetone and concentrated sulfuric acid (Scheme 4). Alternatively, diacid **22** was obtained from tetraacetate **19** by reaction with aqueous acetone in acidic medium. Diacid **22** was submitted to iododecarboxylation with iodosobenzene diacetate and iodine. Under standard conditions (benzene, two 100 W tunsgten lamps),[19,20] **24** was obtained in 33% yield, much of diacid **22** (49%) being recovered.[12] When this reaction was carried out in CH_2Cl_2 as described before for the synthesis of **20** and after the usual work-up, diiodide **24** was obtained in 42% yield and diacid **22** was recovered in 49% yield. Diacid **22** could be reused without further purification.

Reaction of **24** with *tert*-butyllithium in anhydrous THF at −78°C in the presence of 1,3-diphenylisobenzofuran afforded the expected Diels–Alder adduct **23** in 63% isolated yield. The ^{13}C NMR spectrum of compound **23** at 75.4 MHz is temperature dependent due to the slow rotation of the phenyl groups around the C*ipso*–C1(14) bonds. At 22°C, the C*ortho* and C*meta* phenyl atoms gave broad signals, which became sharper at 50°C (δ C*ortho* 125.7 ppm and δ C*meta* 128.8 ppm). At −50°C, two pairs of sharp signals were observed for the C*ortho* (δ C*ortho* 124.6 and 125.9 ppm) and for the C*meta* (δ C*meta* 127.9 and 129.2 ppm) phenyl atoms. The coalescence temperature for the signals of the C*meta* atoms took place at 30°C, while for the C*ortho* atoms took place at 32°C. From the above data for the C*meta* atoms, a kinetic constant at the coalescence temperature (k_C) of 216 s^{-1} was obtained.[21] From this value and applying the Eyring equation,[21] a free



Scheme 4. Generation and trapping of 5α,6α:11α,12α-bis(isopropylidenedioxy)pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodec-8-ene (**25**). (i) (a) *N*-methylmorpholine *N*-oxide, $K_2OsO_4{\cdot}2H_2O$, *t*-BuOH/H_2O/acetone 1:1:1, room temperature, 23 h, (b) acetone, concentrated H_2SO_4, reflux, 18 h, 84% overall yield (Ref. 12); (ii) Acetone/water 2:1, concentrated H_2SO_4, reflux, 18 h, 93%; (iii) Iodosobenzene diacetate, I_2, CH_2Cl_2, $h\nu$, 4+18 h. **24**:42%, recovered **22**:49%; (iv) 1,3-diphenylisobenzofuran, *t*-BuLi, THF, −78°C, 30 min, 63% (Ref. 12).



Scheme 5. Cross-coupling of highly pyramidalized alkenes **25** and **1b** and reactivity of the derived cyclobutane cross products. (i) Na, 1,4-dioxane, reflux, 4 h:**13b** (37%), **26** (4.3%), **27** (1.2%), **28** (19%), **29** and **30** (55–64%); (ii) Na (Hg), 1,4-dioxane, room temperature overnight, **11b** and **13b** (41.5%), **26** (5.3%), **28** (48%), **29** (52%); (yield of compounds **11b**, **13b**, **26**, and **27** was calculated from starting **10b**, while yield of compounds **28**–**30** was calculated from **24**: ratio **24/10b** of 1:3); (iii) 1,4-dioxane, reflux, 24 h, quantitative yield; (iv) $h\nu$, cyclohexane, 6 h, quantitative yield; (v) 2N aq. HCl, methanol, 75°C, 16 h, 99%; (vi) 1,4-dioxane, reflux, 3 h, quantitative yield; (vii) DMSO, trifluoroacetic anhydride, CH_2Cl_2, −60°C, 2 h, then, Et_3N, −60°C, 90 min, 60%; (viii) neat, 180°C/0.7 Torr, 30 min, quantitative yield. ((i)–(vii)), Ref. 12).

enthalpy of activation of 14.5 kcal mol^{-1} was calculated. Similarly, from the data for the C*ortho* atoms, a k_C of 208 s^{-1} was obtained from which a free enthalpy of activation of 14.7 kcal mol^{-1} was calculated. The difference between the two enthalpy of activation values lies within the experimental error (about 0.2 kcal mol^{-1}).[21b]

Reaction of a mixture of diiodides **24** and **10b** in the molar ratio **24/10b** of 1:3 with excess of melted sodium in refluxing 1,4-dioxane for 4 h gave a mixture of products (Scheme 5) which could be separated by column chromatography (aluminum oxide, hexane/ethyl acetate mixtures), isolating in order of elution: dihydrodimer **26** (4.3% yield from **10b**), diene dimer **13b** (37% yield from **10b**), compound **27**, derived from alkene **1b** and 1,4-dioxane (1.2% yield from **10b**), a mixture of the cross-coupled diene **30** and its isomeric cyclobutane precursor **29** in the approximate ratio of 4:1 (^{1}H NMR) (55% combined yield from **24**, or 18.3% combined yield from **10b**) and the reduction product **28** (19% yield from **24**).[12] Thus, the global yield of compounds derived from **10b** (**13b**, **26**, **27** and **29** plus **30**) amounts 60.8%, while the global yield of compounds derived from **24** (**28** and **29** plus **30**) amounts 74%. Under these conditions (great excess of **10b**), dimers of alkene **25** were not observed. Contrary to our previous experience in the cross-coupling of alkenes **6** and **1a** or **1b**, whose diene or cyclobutane reaction product could not be isolated, the polarity differences among the products of the above reaction, due to the presence in several of them of acetal functions, allowed us to separate the polar cross-coupling products **29** and **30** from the less polar dimers **11b** and **13b** and by-products **26** and **27** and from the more polar product **28**. An improved combined yield of the cross-products **29** and **30** of 64% has recently been obtained by slowing down the polarity increase of the solvent during the column chromatography of the crude reaction mixture.

When the cross-coupling reaction of **24** and **10b** was carried out using the same ratio of reactants and 0.45% sodium amalgam at room temperature, **29** was isolated in 52% yield, the formation of **30** being not observed. This observation suggests that the initially formed product in the cross-coupling of **25** and **1b** is the cyclobutane derivative **29** which under refluxing 1,4-dioxane is thermally transformed into diene **30**. In the above reaction, the formation of dimer **13b** was also observed. However, as expected, dimers of **25** were not detected.

Irradiation of the mixture of **29** and **30** in a quartz reactor using a 125 W medium-pressure mercury lamp in the absence of any photosensitizer, allowed us to obtain pure **29** in quantitative yield. Acid hydrolysis of **29** gave **33** in 99% yield. Compounds **29** and **33** showed to be stable for extended periods of time at room temperature, although they were completely converted thermally to the corresponding diene isomers, **30** and **34**, respectively. Although we were able to fully characterize the above dienes, these compounds showed to be acid-sensitive and must be handled with care.

Swern oxidation of **33** gave the tetrone **32** in 60% isolated

yield. We could purify **32** by column chromatography (aluminum oxide, hexane/ethyl acetate mixtures) and fully characterize it. However, **32** underwent slow [2+2] retrocycloaddition to diene **31** at room temperature. Complete conversion of **32** to **31** was observed after refluxing it in 1,4-dioxane solution for 3 h.

3. Theoretical calculations

In order to achieve a better understanding of the behavior of the cyclobutane derivatives **29**, **32** and **33** and the corresponding isomeric dienes, **30**, **31** and **34**, we carried out Molecular Mechanics (MM2) and ab initio (Gaussian, HF/3-21G)[22] calculations on these compounds and on the parent hydrocarbons **12b** and **14b**.

Firstly, we optimized the geometry of pyramidalized alkene **25** at the HF level using the 3-21G basis set. The minimum-energy nature of this structure was verified from vibrational frequency analysis. The calculated optimized geometry of alkene **25** was very close to the previously reported optimized geometry of the parent alkene **6**.[17] For example, the pyramidalization angle of **25** (61.8°) and the carbon–carbon double bond length (1.356 Å) at this level of theory are almost identical to those of **6** (61.8° and 1.357 Å, respectively). We also calculated the Olefin Strain Energy (OSE) and the Heat of Hydrogenation of **25**. Since ab initio methods do not allow to obtain the strain of a compound in a straightforward manner, the relative OSE of **25** was computed taking bicyclo[3.3.0]oct-1(5)-ene as a reference compound, as previously reported by Borden for **6** and several highly pyramidalized alkenes with the tricyclo[3.3.-n.0^{3,7}]alk-1(5)-ene skeleton.[11h] From the calculated energy of alkene **25** and bicyclo[3.3.0]oct-1(5)-ene as well as of their hydrogenation derivatives we obtained a calculated value for the OSE of **25** of 84.8 kcal mol^{-1}, identical to the value obtained for the parent alkene **6**. The heat of hydrogenation of **25** was calculated as the difference between the heat of formation of **25** and its corresponding alkane taking into account the heat of formation of hydrogen. All the energy values were corrected with the zero-point energy and thermal (298 K) corrections. Once again, the calculated value for the heat of hydrogenation of **25** (119.3 kcal mol^{-1}) was almost identical to that of **6** (119.2 kcal mol^{-1}). We and others have previously found that DFT calculations are probably the most reliable (excluding very expensive MCSCF calculations) for highly pyramidalized alkenes.[17,23] Nevertheless, taking into account the similarity observed at the HF/3-21G level between **25** and **6** (Table 1) and that we had previously studied **6** at the B3LYP/6-31G* level, we did not perform more calculations on this compound.

Next, we optimized the geometry of tetrones **31** and **32** and the parent hydrocarbons **14b** and **12b** at the HF level using the 3-21G basis set. The minimum-energy nature of the optimized structures was verified from vibrational frequency analysis. HF/6-31G*, B3LYP/6-31G* and MP2/3-21G single-point calculations were carried out by using the HF/3-21G optimized geometry in each case. Zero-point energy and thermal (298 K) corrections were determined from the HF/3-21G geometry in each case. Moreover, the differences in energy were also determined from MM2 calculations. For tetrahydroxy compounds **33** and **34** and for acetals **29** and **30**, the differences in energy were determined only from MM2 calculations.

Table 1. Enthalpy of reaction (ΔH_r, kcal mol^{-1}) calculated by Molecular Mechanics (MM2(91)) and ab initio methods and experimental (DSC) for the [2+2] retrocycloaddition of cyclobutane compounds **12b**, **29**, **32** and **33**

Method	Compound			
	12b	**33**	**29**	**32**
HF/3-21G	−16.7	–	–	−26.0
HF/6-31G*	−24.4	–	–	−35.6
MP2/3-21G	−14.7	–	–	−25.7
B3LYP/6-31G*	−24.5	–	–	−35.6
MM2	−24.1	−23.3	−21.0	−36.2
Experimental (DSC)	–	−19.0±0.8	–	−30.7±1.4

Both ab initio and MM2 results (see Table 1) indicate a greater stability for dienes than for the corresponding cyclobutane derivatives. However, irrespective of the method, the enthalpy difference is larger for the conversion of **32** to **31** than for the conversion of **12b** to **14b**. The greater instability of the cyclobutane derivative **32** in front of diene **31** as compared with cyclobutane derivatives **12b**, **29** and **33** is likely related to the relative destabilization of dienes **14b**, **30** and **34** due to the approaching of the 4(5,10,11)-Hβ of the C12 subunit to the 18(20,19,15)-Hβ protons of the C8 subunit during the cyclobutane opening process. Since **31** lacks these destabilizing interactions due to the sp^2 hybridization of the C4(5,10,11) carbon atoms, the retrocycloaddition of

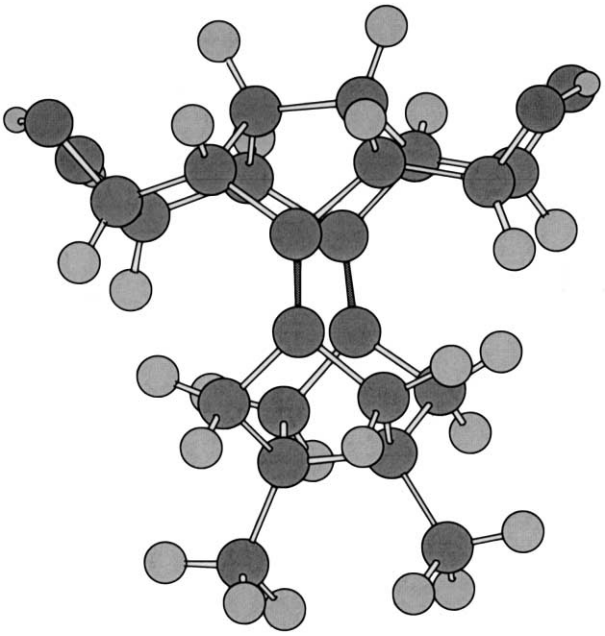


Figure 2. Minimum energy conformation (MM2) and significant structural parameters, distances (d, Å) and dihedral angles (ϑ, degrees), of tetrol **34**. Distances: d(4-Hβ–18-Hβ) 1.90 Å, d(4-Hβ–20-Hβ) 3.52 Å, d(5-Hβ–18-Hβ) 2.48 Å, d(5-Hβ–20-Hβ) 1.85 Å, d(10-Hβ–19-Hβ) 1.84 Å, d(10-Hβ–15-Hβ) 2.43 Å, d(11-Hβ–19-Hβ) 3.58 Å, d(11-Hβ–15-Hβ) 1.92 Å; dihedral angles: ϑ(O–C4–C5–O) −5.8°, ϑ(H–C4–C5–H) −4.0°, ϑ(O–C10–C11–O) −7.6°, ϑ(H–C10–C11–H) −5.1°, ϑ(C19–C1–C2–C3) 175.7°, ϑ(C19–C1–C2–C9) 3.0°, ϑ(C18–C1–C2–C3) 9.4°, ϑ(C18–C1–C2–C9) −163.3°, ϑ(C12–C13–C14–C20) 175.6°, ϑ(C12–C13–C14–C15) 9.0°, ϑ(C6–C13–C14–C20) 3.2°, ϑ(C6–C13–C14–C15) −163.4°.

32 must be more exothermic than that of **12b**, **29** and **33**. In fact, while cyclobutane derivatives **12b** and **32** and diene **31** show minimum energy C_{2v} conformations (ab initio calculations), diene **14b** shows an energy minimum for a C_2 conformation derived from the C_{2v} by slightly twisting around the C=C double bonds and around the C4–C5 and C10–C11 bonds, a fact that greatly contributes to the reduction of the aforementioned destabilizing interactions between the 4(5,10,11)-Hβ and the 18(20,19,15)-Hβ protons. A similar situation was found for tetrol **34** by MM2 calculations. Fig. 2 shows the preferred conformation of diene tetrol **34** (MM2) with indication of significant interatomic distances and dihedral angles to evaluate the magnitude of the above cited twisting.

4. DSC Analysis

The thermal induced conversion of cyclobutanes **32** and **33** to dienes **31** and **34**, respectively, was studied by Differential Scanning Calorimetry.[24] A small amount of sample (0.7–0.8 mg) was placed in a sealed aluminum crucible and was heated at a constant rate (2.5, 5.0, 7.5, 10 and 15 K min^{-1}) from room temperature to a temperature well above the reaction had taken place (493 K), while the heat flow was measured. The heat of reaction was determined from the integration of the heat flow signal over the temperature range where the reaction takes place.

For cyclobutane **32**, the reaction started between 353 and 373 K for heating rates between 2.5 and 15 K min^{-1}, and a reaction enthalpy of -30.7 ± 1.4 kcal mol^{-1} was measured. All the heat flow curves obtained showed a similar shape: heat flow increases slowly to a maximum and then returns rapidly to the base line value, reaction range being between 40 and 50 K. In the temperature range of the analysis (298–493 K) no other thermal phenomenon was observed (Fig. 3). When heating was stopped just after the exothermic process had taken place (423 K) and the obtained sample was analyzed by ^{1}H NMR spectroscopy, diene **31** was the only product observed.

These results are in agreement with force-field calculations carried out with the MM2(91) program which predicts a reaction enthalpy (ΔH_r) of -36.2 kcal mol^{-1} and with ab initio calculations that predicts values for ΔH_r between -25.7 and -35.6 kcal mol^{-1} for the retrocycloaddition process of **32** to **31** (Table 1).

The activation energy of the thermal conversion of cyclobutane **32** to diene **31** was determined from the heat flow curves of the DSC analysis obtained at different heating rates. Applying the isoconversion method of Vyazovkin,[25] in which no kinetic model is assumed, an activation energy of 25.7 ± 0.5 kcal mol^{-1} was obtained. Alternatively, following Ozawa's method which assumes a first order kinetic model,[26] a very similar activation energy of 25.4 ± 0.5 kcal mol^{-1} was obtained.

The kinetics of the transformation of **32** to **31** was also followed by ^{1}H NMR in C_6D_6 solution at 50 and 70°C. The ratio **32/31** was easily obtained by integration of the clearly resolved 3(6,9,12)-H signals of both compounds.

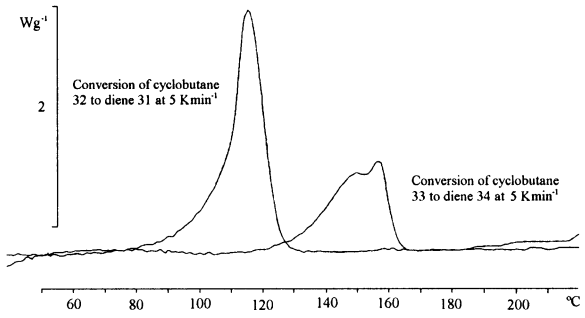


Figure 3. DSC diagrams (heating rate: 5 K min^{-1}; reaction heat: W g^{-1}) for the conversion of cyclobutane **32** to diene **31** and of cyclobutane **33** to diene **34**.

The plot of ln [**32**] vs time for both temperatures gave straight lines (first order kinetics) (r^2=0.991, n=14 for the process at 50°C and r^2=0.998, n=19 for the process at 70°C) with rate constant values of $k_{50}=3.33\times10^{-4}$ and $k_{70}=1.94\times10^{-3}$ min^{-1}. From these rate constant values, by using the Arrehnius equation, an activation energy of 19.4 kcal mol^{-1} was calculated. This value is in apparent contrast with the activation energy of 22.7 kcal mol^{-1} previously obtained[5] for the conversion of cyclobutane **11b** to diene **13b** in $CDCl_3$ solution, a process that is faster ($k_{50}=5.29\times10^{-3}$ min^{-1}) than the conversion of **32** to **31**. However, the rate constant depends not only on the activation energy and the temperature but also on the Arrehnius pre-exponential factor and the solvent, that are different.

Conversion of cyclobutane **33** to diene **34** took place at higher temperatures than the corresponding conversion of cyclobutane **32** to diene **31**. The reaction started between 388 and 410 K for heating rates in the range of 2.5–15 K min^{-1}, and the reaction enthalpy was considerably smaller: -19.0 ± 0.8 kcal mol^{-1} than the value (-30.7 ± 1.4 kcal mol^{-1}) obtained for the conversion of **32** to **31**. The shape of the heat flow curves was substantially different from those obtained for the transformation of **32** to **31**. In this case, an exothermic peak with two maxima was obtained, being, in all cases, the one at higher temperature the absolute maximum. This suggests that the profile obtained is the combination of two overlapping processes. Considering that in the ^{1}H NMR analysis of the sample after the thermal phenomenon had taken place only diene **34** was present, the exothermic peak observed is probably due to the sum of the heat evolved in the conversion of cyclobutane **33** to diene **34** and the heat associated with a conformational change of diene **34**, a fact supported by our ab initio calculations on the model compound **14b** (see above). Unfortunately, for the transformation of **33** to **34**, reliable kinetic data could not be obtained due to the overlapping shape of the heat flow profile.

These results are also in good agreement with force-field calculations carried out with the MM2(91) program which predict a ΔH_r of -23.3 kcal mol^{-1} for the retrocycloaddition process of **33** to **34** (Table 1).

The conversion of cyclobutanes **32** and **33** to dienes **31** and **34**, respectively, is likely a two-step process, which probably takes place through diradical intermediates like the ones derived from the homolytic cleavage of one or

Table 2. Molecular Mechanics (MM2(91)) and ab initio data (distances between the olefinic carbon atoms (d, Å), angle of pyramidalization (Φ, degrees), strain energy (E_{str}, kcal mol^{-1}) and strain energy differences (OSE)) calculated for compounds **14b**, **30**, **31** and **34** and their mono-(diene+H_2) and di-hydrogenated (diene+2H_2) products

Parameter	Compound			
	14b	**30**	**34**	**31**
d_{C2-C13}	2.656 (2.723)	2.594	2.641	2.699 (2.782)
d_{C1-C14}	2.744 (2.852)	2.671	2.734	2.778 (2.864)
Φ_a	8.4 (11.5)	9.1	7.1	6.6 (8.2)
Φ_b	11.8 (15.1)	13.3	10.3	9.9 (11.0)
E_{str} (diene)	92.1	85.4	87.1	60.4
E_{str} (diene+H_2)	109.1	100.7	105.3	77.9
E_{str} (diene+2H_2)	128.9	120.4	126.0	98.4
OSE [diene−(diene+H_2)]	−17.0	−15.3	−18.2	−17.5
OSE [(diene+H_2)−(diene+2H_2)]	−19.8	−19.7	−20.7	−20.5
OSE [diene−(diene+2H_2)]	−36.8	−35.0	−38.9	−38.0

Values in parentheses correspond to ab initio (HF/3-21G) calculated data. Φ_a and Φ_b correspond to the pyramidalization angles of the C2(13) and C1(14) atoms, respectively.

the other of the inner cyclobutane carbon–carbon bonds of the starting compounds.

5. Hyperstability and pyramidalization of dienes 14b, 30, 31 and 34

It is well-known that, in general, the Strain Energy (SE) of a cycloalkene is higher than that of the corresponding cycloalkane, i.e. a cycloalkene usually has a positive Olefin Strain Energy (OSE). However, P. v. R. Schleyer[14] and later other authors,[27] found that several cycloalkenes showed negative OSE values due to an increase in vicinal and transannular hydrogen interactions in the cycloalkane. On the other hand, these alkenes, dubbed 'hyperstable alkenes', show negative values for the difference ΔH_f(alkane) − ΔH_f(alkene), although they are lower than usual. Some time ago, we reported that **13b** was a highly hyperstable and slightly pyramidalized diene.[28] MM2 calculations (see Table 2) show that dienes **14b**, **30**, **31** and **34** are even more hyperstable dienes. This is due to important increases in the torsional and Van der Waals terms because of the small dihedral angles formed by the new C–H bonds and by these bonds and C15(18,19,20)–Hα and C3(6,9,12)–H. Moreover, in **14b**, **34** and **30**, hydrogenation increases the strain between the 4(5,10,11)-Hβ and the 18(20,15,19)-Hβ protons. Interestingly and contrary to **13a** and **13b**,[28] hydrogenation of the second double bond in **14b**, **30**, **31** and **34** raises the strain energy (−19.8, −19,7, −20.7 and −20.5 kcal mol^{-1}, respectively) more than the hydrogenation of the first one (−17.0, −15.3, −18.2 and −17.5 kcal mol^{-1}, respectively). A similar situation was found by Prinzbach in bissecododecahedradienes.[29]

The UV spectrum of dienes **30** and **31** in solution show maximum absorption bands at λ=208 and 201 nm, respectively, a fact that allows their conversion into the corresponding cyclobutane isomers by direct irradiation with UV light in deoxygenated cyclohexane in the absence of any photosensitizer (see above and Section 6). This fact might be due to the pyramidalization of the double bonds which lowers the LUMO and increases the HOMO energies and to through-bond and/or through-space π–π interactions.[30] MM2 and ab initio calculations showed that **14b**, **30**, **31** and **34** are pyramidalized alkenes. Worthy of note, **30** is slightly more pyramidalized than **31** (see Table 2), a fact reflected in the larger wavelength maximum UV absorption. Interestingly, the pyramidalization angle (Φ) is larger for the ab initio than for the MM2 calculations. This fact may be related to a destabilizing transannular π–π repulsion, not taken into account by the MM2 methods, that would explain the lower pyramidalization calculated by this method. A transannular π–π interaction was found for the dienes **13a** and **13b**.[31]

6. Experimental

6.1. General

Melting points were determined with a MFB 595010 M Gallenkamp melting point apparatus. 500 MHz ^{1}H NMR spectra were performed on a Varian VXR 500 spectrometer, 300 MHz ^{1}H- and 75.4 MHz ^{13}C NMR spectra on a Varian Gemini 300, and 50.3 MHz ^{13}C NMR spectra on a Varian Gemini 200. Chemical shifts (δ) are reported in ppm related to internal tetramethylsilane (TMS). IR spectra were recorded on a FT/IR Perkin–Elmer spectrometer, model 1600. Routine MS spectra were taken on a Hewlett–Packard 5988A spectrometer, the sample was introduced directly or through a gas chromatograph, Hewlett–Packard model 5890 Series II, equipped with a 30 m HP-5 (5% diphenyl–95% dimethyl-polysiloxane) column [conditions: 10 psi, initial temperature: 100°C (2 min), then heating at a rate of 10°C min^{-1} till 250°C, then isothermic] and the electron impact technique (70 eV). Only significant ions are given: those with higher relative abundance, except for the ions with higher m/z values. High-resolution mass spectra were recorded on an Autospec-Q mass spectrometer from Micromass using the electron impact technique (70 eV) and direct sample introduction. DSC analysis were performed in a Mettler Toledo DSC-30 equipment using standard 40 μL aluminum crucibles. Silica gel SDS 60 (70–200 μm) was utilized for the column chromatography. NMR and routine MS spectra were performed at the Serveis Científico-Tècnics of the University of Barcelona, while elemental analyses and high resolution mass spectra were carried out, respectively, at the Microanalysis Service and the

Mass Spectrometry Laboratory of the Centro de Investigación y Desarrollo (C.I.D.), C.S.I.C., Barcelona, Spain.

6.1.1. 5α,6α,11α,12α-Tetraacetoxypentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane-8,9-dicarboxylic anhydride (18). To a cold (0°C) solution of *N*-methylmorpholine-*N*-oxide (6.4 g, 54.7 mmol) and $K_2OsO_4{\cdot}2H_2O$ (300 mg, 0.81 mmol) in a mixture of *t*-BuOH/H_2O in the ratio of 1:1 (50 mL), a solution of anhydride **17** (5.0 g, 22.1 mmol) in acetone (25 mL) was added dropwise and the mixture was stirred at room temperature for 23 h (TLC monitoring). The mixture was diluted with H_2O (50 mL) and washed with ethyl acetate (3×25 mL). The aqueous phase was concentrated to dryness in vacuo and the residue (11.3 g) was poured into acetic anhydride (200 mL). The resulting mixture was heated under reflux for 2 h and concentrated in vacuo to give a solid residue (15.67 g) that was dissolved in CH_2Cl_2 (300 mL). The organic phase was washed with H_2O (3×80 mL), dried with anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give crude **18** (10.6 g). The obtained solid was heated under reflux in acetone (800 mL) with activated charcoal (3 g) for 3 h. The mixture was filtered through a pad of Celite® and evaporated to dryness to afford **18** as the monohydrate (9.21 g, 87%), mp 290–291°C (acetone); [Found: C, 55.1; H, 4.8. $C_{22}H_{22}O_{11}{\cdot}H_2O$ requires C, 55.00; H, 5.04%]; ν_{max}(KBr) 3022, 1862, 1823, 1788, 1748, 1362, 1295, 1264, 1248, 1217, 1051, 1024, 923 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 5.12 (s, 4H, 5(6,11,12)-H), 3.20 (broad s, 2H, 2(3)-H), 2.93 (d, *J*=2.5 Hz, 4H, 1(4,7,10)-H), 2.01 (s, 12H, C*H*$_3$CO$_2$); δ_C (75.4 MHz, $CDCl_3$) 169.0 (C, CH_3CO_2), 166.3 (C, 8(9)-COO), 69.7 (CH, C5(6,11,12)), 60.5 (CH, C1(4,7,10)), 57.8 (C, C8(9)), 49.6 (CH, C2(3)), 20.3 (CH_3, CH_3CO_2); *m/z* (EI) 419 [(M−CH_3CO)$^+$, 2], 418 [(M−CH_3COH)$^{\cdot+}$, 5], 403 [(M−CH_3COO)$^+$, 12], 392 [(M−CH_2CO–CO)$^{\cdot+}$, 11], 360 [(M−CH_3COOH–CH_2CO)$^{\cdot+}$, 23], 300 [(M−2CH_3COOH–CH_2CO)$^{\cdot+}$, 18], 288 [(M−CH_3COOH–CH_2CO–CO_2–CO)$^{\cdot+}$, 20], 258 [(M−2CH_3COOH–2CH_2CO)$^{\cdot+}$, 23], 240 [(M−3CH_3COOH–CH_2CO)$^{\cdot+}$, 18], 230 [(M−2CH_3COOH–2CH_2CO–CO)$^{\cdot+}$, 17], 228 [(M−2CH_3COOH–CH_2CO–CO_2–CO)$^{\cdot+}$, 41], 212 [(M−3CH_3COOH–CH_2CO–CO)$^{\cdot+}$, 17], 186 [(M−2CH_3COOH–2CH_2CO–CO_2–CO)$^{\cdot+}$, 94], 169 (45), 168 [(M−3CH_3COOH–CH_2CO–CO_2–CO)$^{\cdot+}$, 100], 129 (45).

6.1.2. 5α,6α,11α,12α-Tetraacetoxypentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane-8,9-dicarboxylic acid (19). To a solution of anhydride **18** hydrate (8.67 g, 18.8 mmol) in THF (200 mL), $NaHCO_3$ saturated aqueous solution (150 mL) was added and the mixture was stirred for 18 h at room temperature. The resulting suspension was diluted with H_2O and washed with CH_2Cl_2 (3×80 mL). The cold (0–5°C) aqueous layer was acidified with aqueous 1N HCl (150 mL) and extracted with ethyl acetate (3×125 mL). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo to give **19** (7.96 g, 92%), mp 282.8–283.4°C (acetone/hexane); [Found: C, 54.9; H, 5.1. $C_{22}H_{24}O_{12}$ requires C, 55.00; H, 5.04%]; ν_{max}(KBr) 3700–2500 (max. at 3288, 3018, 2980), 1736, 1693, 1439, 1414, 1376, 1247, 1151, 1053, 1022, 925, 863, 819, 701 cm^{-1}; δ_H (500 MHz, DMSO-d_6) 5.31 (s, 4H, 5(6,11,12)-H), 2.80 (m, 2H, 2(3)-H),), 2.59 (d, *J*=2.0 Hz, 4H, 1(4,7,10)-H), 1.97 (s, 12H, C*H*$_3$CO$_2$); δ_C (75.4 MHz, DMSO-d_6) 171.1 (C, COOH), 169.4 (C, CH_3CO_2), 70.6 (CH, C5(6,11,12)), 60.0 (CH, C1(4,7,10)), 56.5 (C, C8(9)), 44.8 (CH, C2(3)), 20.6 (CH_3, CH_3CO_2); *m/z* (EI) 463 [(M−OH)$^+$, <1], 421 [(M−CH_3COO)$^+$, 1], 419 [(M−CH_3COOH–H)$^+$, 1], 403 [(M−CH_3COOH–OH)$^+$, 1], 402 [(M−CH_3COOH–H_2O)$^{\cdot+}$, 1], 378 [(M−CH_3COOH–CH_2CO)$^{\cdot+}$, 23], 360 [(M−2CH_3COOH)$^{\cdot+}$, 66], 318 [(M−2CH_3COOH–CH_2CO)$^{\cdot+}$, 50], 300 [(M−3CH_3COOH)$^{\cdot+}$, 78], 258 [(M−3CH_3COOH–CH_2CO)$^{\cdot+}$, 100], 240 [(M−4CH_3COOH)$^{\cdot+}$, 57], 230 [(M−3CH_3COOH–CH_2CO–CO)$^{\cdot+}$, 24], 214 (26), 212 [(M−4CH_3COOH–CO)$^{\cdot+}$, 41], 186 [(M−3CH_3COOH–CH_2CO–CO_2–CO)$^{\cdot+}$, 31], 169 [(M−3CH_3COOH–CH_3COO–CO_2–CO)$^+$, 32], 168 [(M−4CH_3COOH–CO_2–CO)$^{\cdot+}$, 29].

6.1.3. 5α,6α,11α,12α-Tetraacetoxy-8,9-diiodopentacyclo-[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane (20). A suspension of diacid **19** (325 mg, 0.68 mmol), iodosobenzene diacetate (480 mg, 1.5 mmol) and iodine (378 mg, 1.5 mmol) in anhydrous CH_2Cl_2 (10 mL) was irradiated under reflux with a 60 W tungsten lamp for 4 h. The mixture was allowed to cool to room temperature, more iodosobenzene diacetate (480 mg, 1.5 mmol) and iodine (378 mg, 1.5 mmol) were added and irradiation under reflux was continued for 18 h more. The cold (room temperature) solution was diluted with CH_2Cl_2 (15 mL), washed with 10% aqueous solution of sodium thiosulfate (3×10 mL), saturated $NaHCO_3$ aqueous solution (3×10 mL) and brine (2×10 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo to give a residue (210 mg) which was submitted to column chromatography (silica gel, hexane/ethyl acetate mixtures). On elution with an hexane/ethyl acetate mixture in the ratio of 55:45, pure **20** (104 mg, 24%) was obtained as a white solid. On elution with a mixture of the same solvents in the ratio of 35:65, anhydride **18** (36 mg, 11%) was isolated.

The above sodium thiosulfate aqueous layer was extracted with ethyl acetate (3×20 mL). The organic extracts were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo to give 30 mg (9%) of diacid **19**.

The $NaHCO_3$ aqueous layer was acidified with concentrated HCl and extracted with ethyl acetate (3×20 mL). The organic extracts were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo to give 160 mg (49%) of diacid **19** (58% global yield of recovered **19**).

Analytical and spectroscopic data of compound **20**: mp 282.2–283.5°C (hexane/ethyl acetate); [Found: C, 37.3; H, 3.5; I, 39.3. $C_{20}H_{22}I_2O_8$ requires C, 37.29; H, 3.44; I, 39.40%]; ν_{max}(KBr) 2974, 2957, 1743, 1430, 1375, 1360, 1232, 1098, 1054, 1023, 940, 912, 836 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 5.32 (s, 4H, 5(6,11,12)-H), 2.76 (m, 2H, 2(3)-H), 2.49 (d, *J*=3.0 Hz, 4H, 1(4,7,10)-H), 2.05 (s, 12H, C*H*$_3$CO$_2$); δ_C (75.4 MHz, $CDCl_3$) 169.4 (C, CH_3CO_2), 73.1 (CH, C5(6,11,12)), 65.2 (CH, C1(4,7,10)), 51.1 (C, C8(9)), 44.1 (CH, C2(3)), 20.5 (CH_3, CH_3CO_2); *m/z* (EI) 584 [(M−CH_3COOH)$^{\cdot+}$, 15], 524 [(M−2CH_3COOH)$^{\cdot+}$, 48], 482 [(M−2CH_3COOH–CH_2CO)$^{\cdot+}$, 34], 464 [(M−3CH_3COOH)$^{\cdot+}$, 100], 422 [(M−3CH_3COOH–CH_2CO)$^{\cdot+}$, 29], 355 [(M−2CH_3COOH–CH_2CO–I)$^{\cdot+}$, 27], 313 [(M−2CH_3COOH–2CH_2CO–I)$^{\cdot+}$, 59], 295 [(M−3CH_3COOH–CH_2CO–I)$^{\cdot+}$, 70], 186 [(M−2CH_3COOH–2CH_2CO–2I)$^{\cdot+}$,

40], 168 [$(M-3CH_3COOH-CH_2CO-2I)^{\cdot+}$, 31], 157 (50), 129 (59), 128 (54), 115 (48).

6.1.4. Attempted cross reaction of pentacyclic diiodide 20 and tricyclic diiodide 11b with melted sodium: isolation of 3,3′,7,7′-tetramethyl-1,1′-bi(tricyclo[3.3.0.0^{3,7}]octyl) (22), 4,5,10,11-tetramethylpentacyclo[8.2.1.1^{2,5}.1^{4,7}.1^{8,11}]-hexadeca-1,7-diene (13b) and 8,9-diiodopentacyclo-[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane-5α,6α,11α,12α-tetrol (21). A mixture of freshly cut sodium (643 mg, 28 mmol) in anhydrous 1,4-dioxane (5 mL) was heated under reflux until sodium melted. Then, a mixture of diiodides **20** (150 mg, 0.23 mmol) and **10b** (271 mg, 0.70 mmol) was added at once and the mixture was heated under reflux for 4 h. The resulting suspension was allowed to cool to room temperature and was filtered through Celite®. The solid material was washed with hot 1,4-dioxane (2×2 mL) and the combined organic phases were concentrated in vacuo to give **13b** (70 mg, 75%). The solid material was then washed with H_2O and the aqueous phase was extracted with ethyl acetate (3×5 mL), the combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo to give **21** (80 mg, 72%), mp >320°C (methanol/ethyl acetate); ν_{max} (KBr) 3329, 2993, 2971, 2950, 2934, 1394, 1284, 1266, 1236, 1214, 1170, 1150, 1087, 1054, 1011, 933, 906, 852, 818, 800, 776 cm^{-1}; δ_H (500 MHz, CD_3OD) 4.86 (s, mobile H), 4.13 (s, 4H, 5(6,11,12)-H), 2.62 (m, 2H, 2(3)-H), 2.32 (m, 4H, 1(4,7,10)-H); δ_C (75.4 MHz, DMSO-d_6) 70.9 (CH, C5(6,11,12)), 67.3 (CH, C1(4,7,10)), 55.8 (C, C8(9)), 42.1 (CH, C2(3)); *m/z* (EI) 476 ($M^{\cdot+}$, 6), 417 [$(M+H-C_2H_4O_2)^{\cdot+}$, 33], 399 [$(M-C_2H_4O_2-OH)^{\cdot+}$, 43], 272 [$(M-C_2H_4O_2-OH-I)^{\cdot+}$, 15], 145 [$(M-C_2H_4O_2-OH-2I)^{\cdot+}$, 23], 144 [$(M-C_2H_4O_2-H_2O-2I)^{\cdot+}$, 20], 116 (43), 115 (65), 91 (48), 77 (67), 65 (45), 60 (100), 53 (42), 51 (50); HRMS (EI): $M^{\cdot+}$, found 475.8983. $C_{12}H_{14}I_2O_4$ requires 475.8982.

6.1.5. 5α,6α:11α,12α-Bis(isopropylidenedioxy)pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane-8,9-dicarboxylic acid (22) from 19. To a suspension of diacid **19** (4.0 g, 8.33 mmol) in a mixture of acetone/water in the ratio of 2:1 (60 mL), concentrated sulfuric acid (4.2 mL) was added and the mixture was refluxed for 18 h. The cold (room temperature) solution was treated with aqueous 5N NaOH solution (45 mL) and washed with CH_2Cl_2 (3×25 mL). The basic aqueous phase was acidified with concentrated HCl (5 mL) at 0–5°C and the precipitated diacid was filtered, washed with water and dried in vacuo at 60°C to give **22** (2.01 g). The filtrate was extracted with ethyl acetate (3×40 mL) and the organic extracts were dried with anhydrous Na_2SO_4 and concentrated to dryness to afford more **22** (1.02 g, total 3.03 g, 93% overall yield).

6.1.6. 16,17-Dimethylheptacyclo[14.2.1.1^{14,17}.0^{2,9}.0^{3,7}.0^{6,13}.0^{8,12}]icosa-1,13-diene-4α,5α,10α,11α-tetrol (34). Tetrol **33** was heated in vacuo (0.7 Torr) from room temperature to 180°C and maintained at this temperature for 30 min affording the corresponding diene **34** quantitatively, mp >330°C (dec.); [Found: C, 72.9; H, 7.9. $C_{22}H_{28}O_4 \cdot 1/4H_2O$ requires C, 73.20; H, 7.96%]; ν_{max} (KBr) 3420 (O–H st), 3056, 2958, 2893, 2871, 1636, 1400, 1252, 1170, 1034, 968, 910, 734 cm^{-1}; δ_H (500 MHz, CD_3OD) 5.58 (s, 4H, 4(5,10,11)-H), 4.86 (mobile H, 4OH), 3.01 (broad d, *J*=12.5 Hz, 4H, 15(18,19,20)-Hβ), 2.99 (dt, *J*=2.0 Hz, *J*′=5.0 Hz, 2H, 7(8)-H), 2.84 (broad dd, *J*=5.0 Hz, *J*′=1.5 Hz, 4H, 3(6,9,12)-H), 1.90 (broad d, *J*=12.5 Hz, 4H, 15(18,19,20)-Hα), 1.05 (s, 6H, 16(17)-CH_3); δ_C (75.4 MHz, CD_3OD) 134.0 (C) and 133.6 (C)(C2(13) and C1(14)), 74.4 (CH, C4(5,10,11)), 64.8 (CH, C3(6,9,12)), 47.6 (CH_2, C15(18,19,20)), 44.9 (CH, C7(8)), 39.1 (C, C16(17)), 24.4 (CH_3, 16(17)-*C*H_3); *m/z* (EI) 356($M^{\cdot+}$, 3), 225 (4), 223 (4), 143 (21), 129 (31), 128 (27), 115 (29), 107 (25), 105 (30), 91 (54), 77 (46), 57 (45), 55 (100).

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