Pergamon

Tetrahedron 54 (1998) 4679–4696

TETRAHEDRON

Highly Pyramidalized Tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene and Related Compounds: High-Level *Ab Initio* Study, Synthesis and Trapping of Tetracyclo[5.2.1.0^{2,6}.0^{3,8}]dec-7-ene, and Cross-Coupling Reactions

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In memoriam of the late Prof. Dr. Felix Serratosa, who made P. C. and X. S. love organic synthesis and the aesthetics of polyhedranes and organic structural analysis, respectively.

Received 10 February 1998; accepted 19 February 1998

Abstract: The geometries, olefin strain energies, heats of hydrogenation and relative HOMO/LUMO energies of tricyclo [3.3.0.0^{3,7}]oct-1(5)-ene and related compounds have been obtained by *ab initio* calculations using different basis sets. Tetracyclo-[5.2.1.0^{2,6}.0^{3,8}]dec-7-ene, a new member of this series of highly pyramidalized alkenes, has been generated and trapped as different Diels-Alder adducts; in the absence of a trapping agent, it gives the expected dimeric derivatives in a non-stereoselective way and in low yield. For the first time, good yield cross-coupling reactions among highly pyramidalized alkenes have been carried out. The structure of a tetrasecododecahedrane diepoxide derived from a cross-coupled product has been established by X-Ray diffraction analysis.

keywords: Cycloadditions; Polycyclic aliphatic compounds; Strained compounds; X-Ray crystal structures.

Some time ago, we described the synthesis, chemical trapping and dimerization of 3,7-dimethyltricyclo [3.3.0.0^{3,7}]oct-1(5)-ene,[1] **2**, a dimethyl derivative of the most pyrimidalized member of a series of tricyclo[3.3.n.0^{3,7}]alk-1(5)-enes, several members of which had been previously prepared by Borden *et al.*[2-10] (Figure 1). Later, we published the preparation and corresponding reactions of the parent alkene,[11] **1**, the X-ray diffraction analyses of the cyclobutane dimer **4**, and its [2+2] retrocycloaddition product, **6**, as well as a DSC analysis of the conversion of **4** to **6**.[12] Moreover, the hyperstability and some reactivity of dienes **5** and **6** were also published.[13]

PII: S0040-4020(98)00185-9

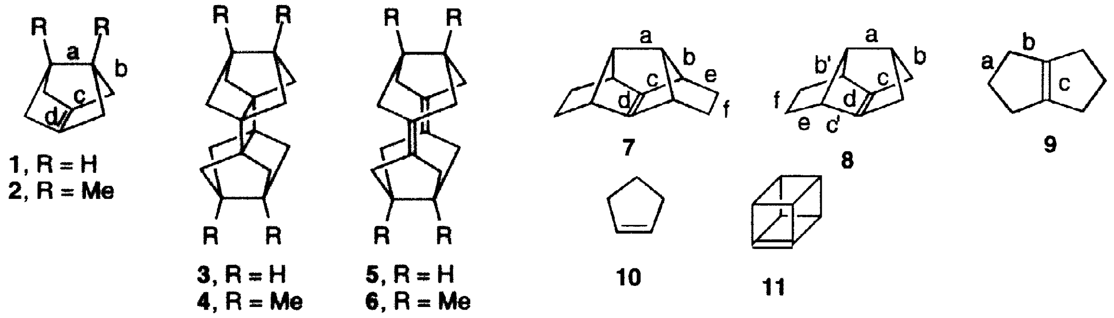


Figure 1. Tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene, **1**, and related compounds.

Several years ago, Hrovat and Borden[14] carried out *ab initio* quantum mechanical calculations on a series of tricyclo[3.3.n.0^{3,7}]alk-1(5)-enes for n = 0, 1, 2 and 3. In addition to the energies of HOMO / LUMO, they computed the olefin strain energies (OSE's) and relative hydrogenation energies, which were determined by single point calculations at the HF/6-31G* and TCSCF/6-31G* levels using the HF/3-21G optimized geometries.

In this paper we describe *ab initio* calculations of the highly pyramidalized alkene **1**, its 3,7-dimethyl derivative, **2**, and their bis-ethano and mono-ethano bridged-compounds **7** and **8**, respectively. Bis-ethano derivative **7** had been previously described,[15] while the synthesis and trapping of alkene **8** and some cross-coupling reactions among **1** or **2** and **7** are herein described for the first time.

Computational Methods

Ab initio calculations were performed with the Gaussian 94 program[16] on an IBM SP/2 computer. Geometry optimizations of pyramidalized alkenes and their corresponding hydrogenation products were carried out at the HF, MP2 and B3LYP levels using the 3-21G and 6-31G* basis sets. The minimum-energy nature of the optimized structures was verified from vibrational frequency analysis. HOMO/LUMO two-configuration TCSCF/6-31G* calculations were also performed.

Results and Discussion

A. Geometries

Tables 1-5 show the carbon-carbon lengths for the ring bonds and the pyramidalization angles of the olefinic carbon atoms of the tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene derivatives **1**, **2**, **7** and **8** and the model bicyclic compound **9**, optimized at the different levels of theory. In the case of **7**, the harmonic vibrational frequencies could not be obtained using the MP2/6-31G* method due to computer limitations. For a given compound, taking the HF/6-31G* results as the reference, slightly overestimated carbon-carbon single bond lenghts (0.007-0.026 Å) and essentially the same value for the carbon-carbon double bond lenghts and pyramidalization angles were observed by using the HF/3-21G method. It is well-known that the MP2 method usually underestimates the single carbon-carbon bond lengths and overestimate the double and triple ones. In the case of tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene derivatives, longer carbon-carbon double bond lenghts (about 0.045 Å) and pyramidalization angles (1.5-1.7 °) were calculated using this method, but only small deviations were observed for the carbon-carbon single bonds. Using the B3LYP/6-31G* calculations, the values obtained for the carbon-carbon double bond lengths and pyramidaliztion angles were intermediate among those obtained by using HF and MP2 methods, while the carbon-carbon single bond lenghts were slightly overestimated (0.006-0.026 Å). Recently, Allinger *et al.*[17] found that the B3LYP method, in general, gives slightly better results than the MP2 for molecules containing only first-row elements and hydrogen.

Two features of the optimized geometries of alkenes **1**, **2**, **7** and **8** are the very similar: a) pyramidalization angles, and b) carbon-carbon double bond lengths (about 1.35 Å for the HF, 1.41 Å for the MP2 and 1.38 Å for the B3LYP methods, respectively). Worthy of note, the *a* bond of these alkenes is quite long (> 1.615 Å), especially in the case of **2** (about 1.68-1.70 Å, depending on the method). These longer bonds may be due to the strain of the tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene substructure present in all of these compounds. The increased lenght in the case of **2** can be associated with a reduction of the interaction between the eclipsed methyl groups. Experimental values for the corresponding carbon-carbon bond lengths in **4**, **6** and a Diels-Alder adduct derived from **2** were obtained by X-ray diffraction analysis,[1,12] which were in good agreement with calculations. Moreover, the TCSCF procedure of Gaussian 94 provides the coefficients of the two configurations for the carbon-carbon double bond, from which the following percentages of diradical character were deduced: **1** (11.0%), **2** (10.5%), **7** (10.7%) and **8** (10.9%). These results show that these alkenes, in spite of their high degree of pyramidalization, are stronger than anti-Bredt alkenes, like some homocubenes[18,19] and dehydroquadricyclanes,[20] which show much higher percentages of diradical character. A similar percentage of diradical character was calculated for two dehydroprismanes.[21]

Table 1
Calculated optimized geometries[a] of alkene **1**.

Method	Bond *a*	Bond *b*	Bond *c*	Bond *d*	Φ
HF/3-21G	1.673	1.590	1.546	1.355	61.2
HF/6-31G*	1.649	1.570	1.531	1.352	61.3
MP2/6-31G*	1.648	1.528	1.529	1.406	62.9
B3LYP/6-31G*	1.667	1.577	1.537	1.380	61.9

[a] Bond lengths (Å) and pyramidalization angles Φ (°).

Table 2
Calculated optimized geometries[a] of alkene **2**.

Method	Bond *a*	Bond *b*	Bond *c*	Bond *d*	Φ
HF/3-21G	1.691	1.590	1.542	1.355	61.3
HF/6-31G*	1.678	1.574	1.526	1.351	61.2
MP2/6-31G*	1.676	1.571	1.525	1.406	62.8
B3LYP/6-31G*	1.704	1.583	1.532	1.380	61.7

[a] Bond lengths (Å) and pyramidalization angles Φ (°).

Table 3
Calculated optimized geometries[a] of alkene **7**.

Method	Bond *a*	Bond *b*	Bond *c*	Bond *d*	Bond *e*	Bond *f*	Φ
HF/3-21G	1.641	1.599	1.542	1.357	1.529	1.555	61.8
HF/6-31G*	1.615	1.581	1.530	1.353	1.522	1.542	61.9
B3LYP/6-31G*	1.625	1.592	1.537	1.382	1.528	1.545	62.4

[a] Bond lengths (Å) and pyramidalization angles Φ (°).

Table 5
Calculated optimized geometries[a] of alkene **9**.

Method	Bond *a*	Bond *b*	Bond *c*	Φ
HF/3-21G	1.572	1.511	1.315	3.8
HF/6-31G*	1.553	1.504	1.317	5.0
MP2/6-31G*	1.551	1.501	1.344	7.9
B3LYP/6-31G*	1.561	1.505	1.337	5.9

[a] Bond lengths (Å) and pyramidalization angles Φ (°).

Table 4
Calculated optimized geometries[a] of alkene **8**.

Method	Bond *a*	Bond *b*	Bond *b'*	Bond *c*	Bond *c'*	Bond *d*	Bond *e*	Bond *f*	Φ[b]
HF/3-21G	1.657	1.587	1.602	1.545	1.544	1.356	1.528	1.553	61.5
HF/6-31G*	1.632	1.567	1.584	1.529	1.532	1.352	1.521	1.539	61.6
MP2/6-31G*	1.632	1.565	1.583	1.528	1.529	1.407	1.520	1.541	63.1
B3LYP/6-31G*	1.645	1.574	1.595	1.536	1.534	1.381	1.526	1.548	62.3

[a] Bond lengths (Å) and pyramidalization angles Φ (°).

[b] Averaged values among those obtained considering whether the *dc* or the *dc'* α angles.

B. Olefin Strain Energies (OSE)

Since *ab initio* methods do not allow to obtain in a straightforward manner the strain of a compound as in Molecular Mechanics methods, the relative olefin strain energies[22,23] of alkenes **1**, **2**, **7** and **8** were computed taking bicyclo[3.3.0]oct-1(5)-ene, **9**, as the reference compound, as previously reported by Hrovat and Borden.[14]

From the calculated energies of alkenes **1**, **2**, **7** and **8**, the reference alkene **9**, as well as of their hydrogenation derivatives (Table 6), and applying equation 1, the OSE of **1**, **2**, **7** and **8** were obtained (Table 7) for each method.

Equation 1 $$\text{OSE(alkene)} = [E(\text{alkene}) - E(\text{alkane})] - [E(\mathbf{9}) - E(\mathbf{9\text{-}H_2})]$$

As can be seen from Table 7, HF/3-21G and HF/6-31G* results are very similar and differ by about 15 kcal mol^{-1} from the OSE values computed at the TCSCF, MP2 and B3LYP levels. For a given method, the OSE's of all of these compounds are very similar as expected taking into account the presence in all of them of the tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene substructure. Very recently, Eaton *et al.*[24] described the experimental OSE value of cubene (63 ± 4 kcal mol^{-1}) which was in good agreement with the value (58.9 kcal mol^{-1}) previously calculated by Hrovat and Borden[14] with a two-configuration wave function (TCSCF/6-31G*//HF/3-21G). The above calculated OSE of cubene is very close to the values obtained in this work using the TCSCF/6-31G*//HF/6-31G* (58.7 kcal mol^{-1}) and HF/6-31G*//HF/6-31G* (66.3 kcal mol^{-1}) methods. In spite of the reasonable agreement between the experimental and calculated values, the calculated ones should be taken with care since the reference compound **9** may not be a good model in this case.[14]

Table 6

Calculated energies (hartrees) of alkenes **1**, **2**, **7**, **8** and **9** and their hydrogenation products.

Compound	HF/3-21G	HF/6-31G*	TCSCF/6-31G*[a]	MP2/6-31G*	B3LYP/6-31G*
1	-306.8577	-308.5606	-308.6092	-309.6217	-310.6854
1-H$_2$	-308.1863	-309.8850	-	-310.9324	-312.0304
2	-384.5054	-386.6376	-386.6868	-387.9704	-389.3229
2-H$_2$	-385.8299	-387.9588	-	-389.2772	-390.6638
7	-459.8417	-462.3929	-462.4414	-	-465.5428
7-H$_2$	-461.1672	-463.7123	-	-	-466.8832
8	-383.3501	-385.4773	-385.5264	-386.7979	-388.1145
8-H$_2$	-384.6771	-386.7992	-	-388.1066	-389.4574
9	-308.1980	-309.9185	-309.9438	-310.9503	-312.0633
9-H$_2$	-309.3884	-311.1026	-	-312.1469	-313.2892

[a] The TCSCF/6-31G* energies were calculated by using the HF/6-31G* optimized geometries.

Table 7

Olefin Strain Energies (OSE, kcal mol^{-1}) calculated for alkenes **1**, **2**, **7** and **8** as the difference between the hydrogenation energy of each alkene and that of the reference compound **9**.

Compound	HF/3-21G	HF/6-31G*	TCSCF/6-31G*	MP2/6-31G*	B3LYP/6-31G*
1	86.7	88.0	73.4	71.6	74.7
2	84.1	86.0	71.0	69.1	72.2
7	84.8	84.9	70.3	-	73.4
8	85.7	86.5	71.5	70.3	73.4

To the best of our knowledge, the calculated OSE's of alkenes **1**, **2**, **7** and **8** are the highest ones described for bridgehead alkenes for which experimental evidence for their generation has been obtained.[14,24,25]

C. Heats of Hydrogenation.

The heats of hydrogenation of the highly pyramidalized alkenes **1**, **2**, **7** and **8** as well as the reference compounds **9**, cyclopentene, **10**, and cubene, **11**, (Table 8) were calculated as the difference between the heats of formation of each alkene 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.

In order to check the results, the heat of hydrogenation of cyclopentene, **10**, was also calculated using the different calculation methods, which were compared with the experimental value.[26] The best results were obtained by using the MP2/6-31G* and B3LYP/6-31G* methods (-26.2 and -27.7 kcal mol^{-1}, respectively, *vs* an experimental value of -26.8±0.2 kcal mol^{-1}) while the TCSCF/6-31G*//HF/6-31G* method gave a highly underestimated value (-13.3 kcal mol^{-1}). All of the HF methods gave overestimated values, although that obtained with the HF/6-31G* method (-29.9 kcal mol^{-1}) was only slightly higher than the experimental one.

The heats of hydrogenation of the model alkene **9** using the different methods were very close to those obtained for **10**, although in this case no experimental datum is available.

However, hydrogenation of strained alkenes is not an ideal process due to the considerable changes that experience the implicated bonds. Wiberg *et al.*[27] found that the HF calculated enthalpies of hydrogenation of a series of strained alkenes were overestimated by 6 ± 2 kcal mol^{-1} using the HF/6-31G* method. The errors were similar when other basis sets were used. Recently, Eaton *et al.*[24] reported the experimental value of the heat of hydrogenation of cubene, **11**, a highly strained alkene, which may serve as a better model than **10** to check our results. The calculated heats of hydrogenation of **11** (Table 8) show that HF/6-31G* method gave slightly overestimated values which are comprised within the limits established by Wiberg *et al.* for other strained alkenes, while the HF/3-21G results are clearly overestimated. The rest of methods gave highly underestimated values. Thus, although for the unstrained alkene **10**, MP2/6-31G* and B3LYP/6-31G* methods give more accurate values than HF methods, in the case of strained alkenes, the best results, although slightly overestimated, seems to be obtained with the HF/6-31G* method.

Table 8
Heats of hydrogenation (kcal mol^{-1}) calculated for alkenes **1**, **2**, **7**, **8** and **9**.

Compound	HF/3-21G	HF/6-31G*	TCSCF/6-31G* //HF/6-31G*[a]	MP2/6-31G*	B3LYP/6-31G*
1	-121.0	-116.0	-85.5	-96.8	-99.1
2	-118.3	-113.9	-83.1	-94.4	-96.5
7	-119.2	-112.9	-82.5	-	-96.3
8	-120.1	-114.6	-83.7	-95.7	-97.8
9	-34.8	-28.5	-12.7	-25.8	-24.8
10[b]	-32.4	-29.9	-13.3	-26.2	-27.7
11[c]	-109.2	-94.7	-71.2	-70.7	-77.4

[a] The TCSCF/6-31G*//HF/6-31G* energies of alkenes and the HF/6-31G*//HF/6-31G* energies of alkanes were used.
[b] Experimental value: - 26.8±0.2 kcal mol^{-1}.
[c] Experimental value: - 90 ± 4 kcal mol^{-1}.

In comparing the heats of hydrogenation calculated for alkenes **1**, **2**, **7** and **8**, a general trend is observed: the heat of hydrogenation decreases in going from the parent alkene **1** to the monoethano-bridged compound **8** and the bisethano-bridged compound **7**. Also, the heat of hydrogenation of the dimethyl derivative **2** is lower than that of **1**. The lower heat of hydrogenation of **7** and **8** *vs* **1** may reflect a relative stabilization of these alkenes due to the ethano bridges which can contribute to release part of the strain. However, the lower heat of hydrogenation of alkene **2** *vs* **1** may reflect the relative destabilization of **2-H$_2$** vs **2** in comparison with **1-H$_2$** *vs* **1**, due to the approaching of the eclipsed methyl groups in **2-H$_2$**. The calculated C3-C7 bond distance in **2** (Table 2, bond *a*) varies from 1.676 to 1.704 Å depending on the level of calculation. The corresponding experimental bond distance (X-ray diffraction analysis) in a Diels-Alder adduct derived from **2**,[12] which contains the tricyclo[3.3.0.0^{3,7}]octane substructure present in **2-H$_2$**, was 1.622 Å. Consequently, a greater steric interaction between the eclipsed methyl groups in **2-H$_2$** as compared with **2** must be expected due to the shortening of the C3-C7 bond on saturation of the C1-C5 double bond.

D. Relative HOMO and LUMO Energies.

Pyramidalized alkenes show long wavelength UV absorptions.[2-10,28] It is well-known that this bathochromic shift is due to an important decrease of the LUMO and a small increase of the HOMO energies on increasing pyramidalization.[14] The calculated HOMO and LUMO energies of the strained alkenes **1**, **2**, **7** and **8** relative to the corresponding energies of the model compound **9** are collected in Table 9.

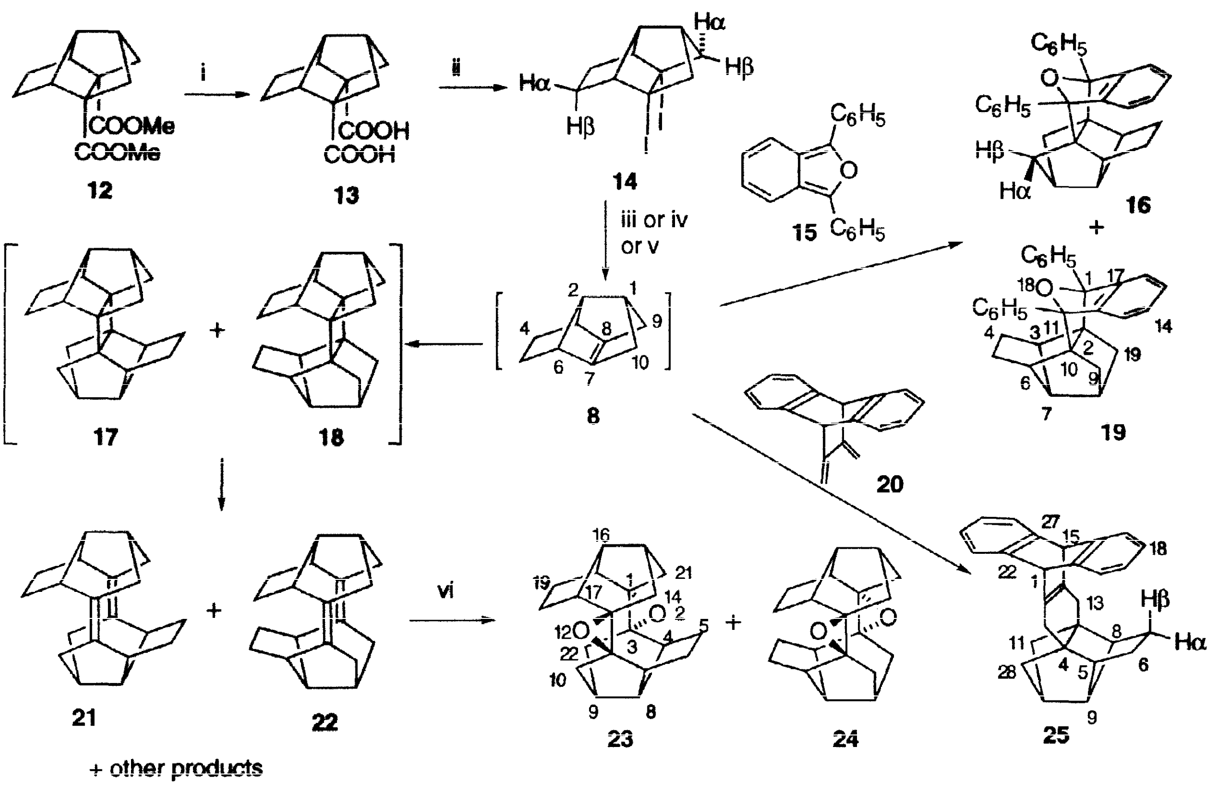
Table 9
Orbital Energies (kcal mol^{-1}) for the HOMO and LUMO of alkenes **1**, **2**, **7** and **8** relative to the energies of the HOMO and LUMO of the reference compound **9**.[a]

Method	Orbital	**1**	**2**	**7**	**8**
HF/3-21G	HOMO	6.4	10.4	9.7	8.1
	LUMO	-67.1	-63.2	-65.5	-66.2
HF/6-31G*	HOMO	9.6	12.4	11.7	10.7
	LUMO	-64.4	-60.9	-63.3	-63.8

[a] The energies of the HOMO / LUMO (kcal mol^{-1}) orbitals for **9** are: -197.8 / 130.0 and -197.3 / 128.4, by using the HF/3-21G and HF/6-31G* methods, respectively.

As can be seen, the HF/6-31G* method gave values for the HOMO/LUMO relative energies of a given compound, which are usually 2 - 3 kcal mol^{-1} higher than the corresponding HF/3-21G values. However, in both methods, for all of these alkenes, the difference between the HOMO and LUMO energies give essentially the same value. From these differences, a rough estimate of the UV absorption maxima corresponding to the HOMO/LUMO transition in these compounds give values as high as about 300 nm, much higher than those observed in the less strained alkenes, tricyclo[3.3.3.0^{3,7}]undec-1(5)-ene (217 ± 5 nm)[8] and tricyclo[3.3.2.0^{3,7}]dec-1(5)-ene (245 ± 15 nm).[6]

Generation and reactions of tetracyclo[5.2.1.$0^{2,6}$.$0^{3,8}$]dec-7-ene (8).



i) KOH, MeOH, H_2O, reflux; ii) $C_6H_5I(OCOCH_3)_2$, I_2, Benzene, hν; iii) **13**, *t*-BuLi, THF, -78 °C; iv) **18**, *t*-BuLi, THF, -78 °C; v) Na, 1,4-Dioxane, reflux; vi) Dimethyldioxirane, acetone, CH_2Cl_2.

Scheme 1. Generation, trapping and dimerization of the highly pyramidalized alkene **8**.

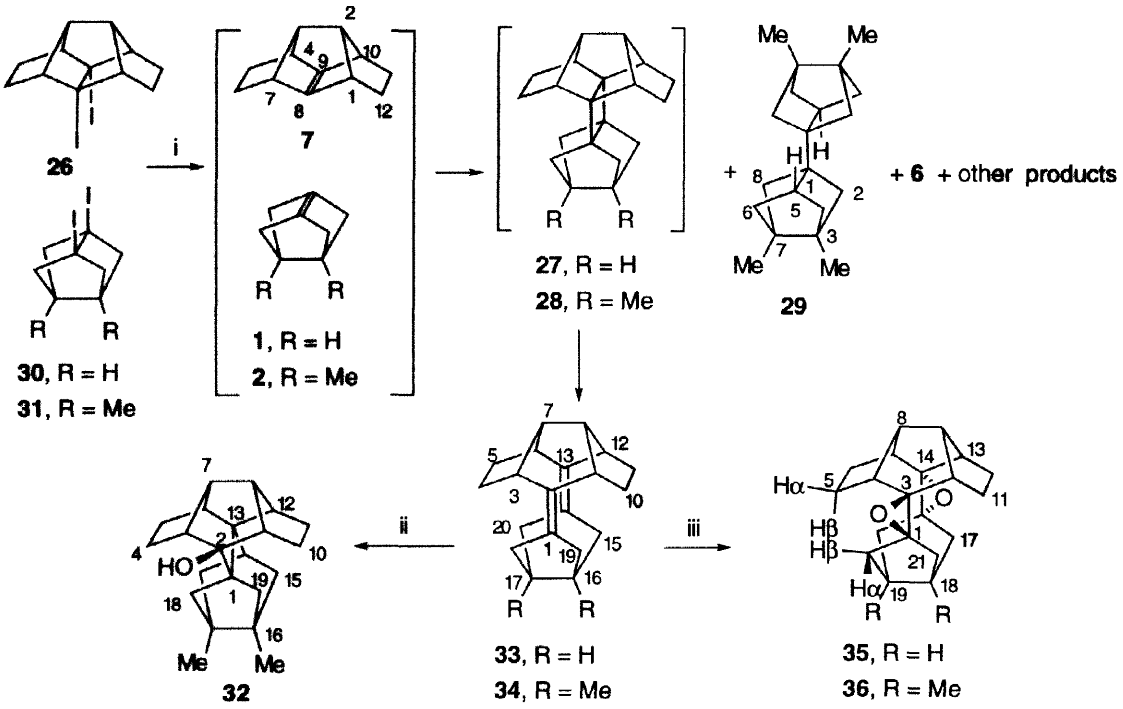
Alkene **8** was generated from the diiodo compound **14**, which was obtained from the known diester **12**.[29] Hydrolysis of diester **12** with 10% potassium hydroxide in methanol gave, after acidification, diacid **13** in high yield. Iododecarboxylation of this compound by using the Moriarty[30] modification of the Suárez[31] procedure, which had been used by our research group to prepare related 1,2-diiodo derivatives,[1,11] let us obtain **14** in 54% isolated yield. Reaction of **14** with *t*-butyllithium in anhydrous THF at -78 °C in the presence of diene **20**[32] gave, after column chromatography, the expected Diels-Alder adduct **25** which was isolated in 48% yield. When a similar reaction was carried out in the presence of 1,3-diphenylisobenzofuran, **15**, a nearly 1:1 mixture of the two stereoisomeric *syn*- and *anti*-adducts, **16** and **19** respectively, was obtained in 77% yield, after column chromatography and crystallization. Although this mixture could not be separated by column chromatography, crystallization from isopropanol gave a mixture slightly enriched in **16**. From the ^1H and ^{13}C NMR spectra of this mixture with the aid of the $^1H/^1H$ homocorrelation and $^1H/^{13}C$ heterocorrelation spectra, the signals corresponding to each stereoisomer could be completely assigned, taking advantage of their different ratio. When **14** was reacted with sodium in boiling dioxane in the absence of a trapping agent, it was obtained a mixture containing (GC/MS), in order of elution, compounds with molecular masses corresponding to: a) a product ($M^{\cdot +}$ = 134) derived from the dihydrodeiodination of **14**, b) a product ($M^{\cdot +}$ = 220) derived from the addition of **8** and dioxane, c) a dihydrodimer of **8** ($M^{\cdot +}$ = 266) whose structure must be related to that of **29** (see later on) and d) two products ($M^{\cdot +}$ = 264) in a ratio close to 1:1, whose molecular mass corresponded to dimers of **8**. According to our previous experience[1,11,12] these dimers must be the diene dimers **21** and **22**, since the corresponding cyclobutane dimers, **17** and **18**, must experience a [2+2] retrocycloaddition process under these reaction conditions. Since column chromatography separation of this mixture was not possible, it was treated with dimethyldioxirane,[33] a reagent able to easily epoxidize highly substituted alkenes.[13] Column chromatography of this new mixture gave in low yield (14%) a mixture of epoxides **23** and **24** which could be spectroscopically characterized. Taking into account the different ratio of both epoxides, the signals of the ^{13}C NMR spectrum of the mixture could be fully assigned to one or the other stereoisomer although it was not possible to differentiate among them.

For a long time[34,35] we considered that dimerization of alkene **8** would give mainly the *anti*-dimer **17** from which diene dimer **21**, a tetrasecododecahedradiene, could be formed. The results herein described showed that this hypothesis was not true. A possible explanation of this fact may be that the highly strained alkene **8** is so reactive that does not discriminate among the transition states leading to the *syn*- and *anti*-cyclobutane dimers, in spite of the great expected steric differences, as it is also the case in the Diels-Alder reaction of **8** with diene **15**. Another possible explanation, according to Eaton,[36] may be that dimerization of highly pyramidalized alkenes such as **8** can take place *via* diradical intermediates, which may explain not only the lack of selectivity but also the formation of partially hydrogenated dimers. Also, according to Borden *et al.*,[8] under the used conditions, the formation of radical anions by electron-transfer from sodium to the alkene **8**, has to be taken into account. The formation of such an intermediate will be favoured by the low-energy LUMO of **8** (see HOMO / LUMO calculations) and may explain the formation of the dihydrodimer and the dihydrodeiodination product. Moreover, the formation of an addition product of **8** and dioxane could be easily explained taking into account the diradical character of **8**, which was calculated to be about 11% (see above under geometries). Much work will be required in the near future to elucidate the mechanistic pathways involved in the reactions of highly pyramidalized alkenes.

Cross-coupling reactions of tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene, 1, and its 3,7-dimethyl derivative 2, with pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodec-8-ene (7).

As an alternative route to tetrasecododecahedrane derivatives which obviates the problem of the *syn* / *anti* dimerization observed with alkene **8**, we planned the cross-coupling reaction of the highly pyramidalized tricyclic alkenes **1** or **2** and the pentacyclic alkene **7** (scheme 2). Much work has been done on the synthesis, trapping and dimerization of highly pyramidalized alkenes.[1-15,37,38] Worthy of note is the recent generation and dimerization of cubene,[36] which is formally followed by two [2+2] retrocycloaddition reactions. However, to the best of our knowledge, a cross-coupling reaction between two highly pyramidalized alkenes has not been described yet.

Alkene **7** was previously generated from diiodide **26** by reaction with *t*-butyllithium and trapped as a Diels-Alder adduct with 1,3-diphenylisobenzofuran.[15] However, dimerization of alkene **7** has not been described yet. Diiodide **26** was previously obtained by iododecarboxylation of the corresponding diacid with red mercury (II) oxide and iodine.[15] In this work, this transformation was better carried out (61% yield) by reacting this diacid with iodosobenzene diacetate and iodine following the Moriarty[30] modification of the Suárez procedure.[31]



i) Na, 1,4-Dioxane, reflux; ii) Silica gel; iii) Dimethyldioxirane, acetone, CH_2Cl_2.

Scheme 2. Cross-coupling reactions of alkenes **1** or **2** and **7**. Synthesis of tetrasecododecahedrane diepoxides **33** and **34**.

Dimerization of alkene **7** to a cyclobutane or diene product, as in the case of alkenes **1** and **2**, must be very difficult due to the great steric interaction between the ethylene bridges of both halves. In our hands, reaction of diiodide **26** with sodium in boiling dioxane gave a complex mixture of products, where several products whose molecular masses corresponded to dimers of **7** were detected by GC/MS although they did not have the expected C_{2v} symmetry of the usual cyclobutane or diene dimers (^{13}C NMR). The steric hindrance for the dimerization of **7**, could favour its cross-coupling reaction with unhindered pyramidalized alkenes such as **1** or **2**.

Reaction of a mixture of diiodides **26** and **31** in the molar ratio **26**/**31** of 1:5 with excess of sodium in refluxing dioxane gave a mixture containing diene **6** as the main component (55% relative area by GC/MS) and minor amounts of a dihydrodimer, **29**, (15% relative area) and the desired cross-coupling diene **30** (16% relative area). Compound **29** had been previously obtained as a minor by-product in the reaction of diiodide **31** with sodium in the absence of a trapping agent. Knowing the NMR signals of **6** and **29**, all of the ^{13}C NMR and some significant ^{1}H NMR signals of **34** could be obtained from the spectra of the mixture. An attempt to isolate the cross-coupling product from this mixture by silica gel column chromatography led to its disappearance, isolating instead a small amount of a compound for which the structure of alcohol **32** was proposed on the basis of its ^{1}H, ^{13}C, ^{1}H/^{1}H homocorrelation, ^{1}H/^{13}C heterocorrelation NMR and MS spectra. The formation of this alcohol can be easily explained from diene **34** through a transannular hydration. Related transannular reactions are well-known in spatially close dienes,[39-43] although dienes **5**[11] or **6**[1,13] are fairly stable compounds. However, the steric interaction between the ethylene bridges of the tetracyclic part and the β-methylene protons of the bicyclic moiety must destabilize dienes **33** or **34**.

To improve the yield of the cross-coupled product, these reactions were better carried out by using an excess of the more readily available diiodide **26**. Reaction of a mixture of **26** and **31** in the molar ratio **26**/**31** of 4:1 with excess of sodium in refluxing dioxane gave a mixture in which the relative area of diene **6** by GC/MS was only 2%. Similarly, when a mixture of **26** and **30** in the molar ratio **26**/**30** of 5:1 was reacted with excess sodium under similar reaction conditions no diene dimer **5** was observed by GC/MS. To avoid hydration of these dienes during isolation, these reduction mixtures were treated with an excess of an acetone solution of dimethyldioxirane (DMD). The new mixtures thus obtained were submitted to silica gel column chromatography which allowed the isolation of the diepoxides **36** and **35**, in fairly good yields of 59 and 64%, respectively, thus confirming the formation of dienes **34** and **33**, probably *via* the corresponding cyclobutane derivatives **28** and **27**, formed by cross-coupling of the highly pyramidalized intermediate alkenes **7** and **1** or **2**. These tetrasecododecahedrane diepoxides were fully characterized spectroscopically and by elemental analysis and, in the case of **35**, by X-Ray diffraction analysis[48] (Figure 2). The ^{13}C NMR spectra of these compounds clearly show their C_{2v} symmetry.

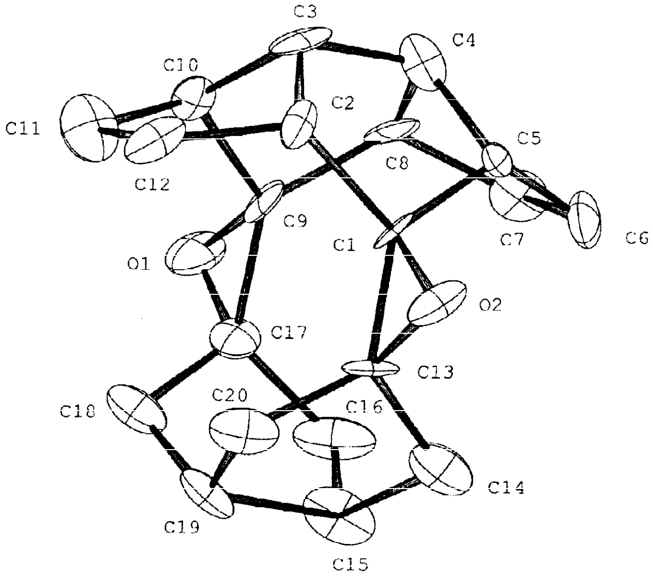


Figure 2. Crystal structure (ORTEP) of diepoxide **35**.

In conclusion, *ab initio* calculations show that the OSE energies of tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene derivatives **1**, **2**, **7** and **8** are higher than those of many other highly pyramidalized alkenes, including cubene. A low (about 11%) diradical character and low-energy LUMO's have also been calculated for these alkenes, which may explain some aspects of their reactivity. The non-concerted nature and the formation of diradicals in the dimerization of **8** may explain the formation of partially hydrogenated dimers and the lack of stereoselectivity in these reactions. The cross coupling reaction of highly pyramidalized alkenes, herein described for the first time, opens an enormous potential in the synthesis of cage compounds. Work is in progress to obtain dienes **33** and **34** in pure form in order to study their transannular and photochemical reactivity. Also, the synthesis of a derivative of **26** functionalized at the ethylene bridges and its cross coupling reaction with **1** or **2** will be started soon.

Experimental

General. Melting points were determined on a MFB 595010 M Gallenkamp melting point apparatus. 500 MHz ^{1}H NMR spectra were performed on a Varian VXR 500 spectrometer, while 300 MHz ^{1}H and 75.4 MHz ^{13}C NMR spectra on a Varian Gemini 300. Except where otherwise stated, ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra at 75.4 MHz, in $CDCl_3$. Chemical shifts (δ) are reported in ppm related to internal tetramethylsilane. Assignments given for the NMR spectra are based on DEPT, ^{1}H/^{1}H and ^{1}H/^{13}C COSY experiments (HMQC sequence). IR spectra were recorded on a FT/IR Perkin-Elmer spectrometer, model 1600. Silica gel SDS 60 (60-200 μm) was usually utilized for the column chromatography. GC/MS were performed on a Hewlett-Packard gas chromatograph, model 5890 Series II, connected to a Hewlett-Packard mass spectrometer HP-5989A, 30-metre HP-5 (5% diphenyl-95% dimethyl-polysiloxane) gas chromatographic column [conditions: 10 psi, initial temperature: 100 °C (1 min), then heating for 9 min at a rate of 8 °C / min (conditions A) or 10 °C / min (conditions B) or 15 °C / min (conditions C) , then isothermic] electron impact, 70 eV. Elemental analyses were carried out at the Microanalysis Service of the *Centro de Investigación y Desarrollo* (C.I.D.), Barcelona, Spain. For *ab initio* calculations the Gaussian 94 (Rev. A. 1) program, run on an IBM SP/2 computer from *Centre de Supercomputació de Catalunya* was used. The systematic names for **16**, **19**, **23**, **24**, **25**, **32**, **35**, and **36** were obtained by using the POLCYC program.[44]

Tetracyclo[5.2.1.0^{2,6}.0^{3,8}]decane-7,8-dicarboxylic acid (**13**). A mixture of diester **12** (112 mg, 0.45 mmol) and a 10% methanolic solution of KOH (5 mL) was heated under reflux for 3 h. Water was added (5 mL) and heating under reflux was continued for 3 h more. The cold mixture was made acidic with conc. HCl and evaporated to dryness in vacuo. The solid residue was extracted with refluxing diethyl ether (5 x 20 mL). The combined organic extracts were dried with anhydrous Na$_2$SO$_4$ and concentrated *in vacuo* giving solid diacid **13** (90 mg, 91% yield), m.p. 220 °C (dec.). IR (KBr) ν: 3600-2200 (OH st), 1696 (C=O st) cm^{-1}. ^{1}H NMR, δ: 1.50 [m, 2 H, 4(5)-Hα], 1.91 [m, 2 H, 9(10)-Hβ), 1.98 [m, 2 H, 9(10)-Hα], 2.10 [m, 2 H, 4(5)-Hβ], 2.38 (m, 1 H, 1-H), 2.41 [m, 2 H, 3(6)-H], 2.47 (m, 1 H, 2-H). ^{13}C NMR, δ: 22.0 [CH$_2$, C4(5)], 34.7 (CH, C1), 50.0 [CH$_2$, C9(10)], 50.7 (CH, C2), 57.8 [CH, C3(6)], 58.7 [C, C7(8)], 179.8 (C, COOH). Anal. Calcd. for C$_{12}$H$_{14}$O$_4$: C, 64.85; H, 6.35. Found: C, 64.90; H, 6.41.

7,8-Diiodotetracyclo[5.2.1.0^{2,6}.0^{3,8}]decane (**14**). A suspension of diacid **13** (188 mg, 0.85 mmol), iodosobenzene diacetate (540 mg, 1.67 mmol) and iodine (425 mg, 1.67 mmol) in anhydrous benzene (55 mL) was irradiated under reflux with two 100 W tungsten-lamps for 4 h. The mixture was allowed to cool to room temperature, more iodosobenzene diacetate (540 mg, 1.67 mmol) and iodine (425 mg, 1.67 mmol) were added and irradiation under reflux was continued for 18 h more. The cold (room temperature) solution was washed with 10% aqueous solution of sodium thiosulfate (3 x 25 mL) and brine (3 x 25 mL), dried with anhydrous Na$_2$SO$_4$ and concentrated *in vacuo* to give an oily residue (405 mg), mixture of iodobenzene and **14**, which was submitted to column chromatography (silica gel, hexane) affording pure **14** (176 mg, 54% yield), m.p. 165-168 °C (hexane). IR (KBr) ν: 2948, 2861, 1454, 1278, 1110, 923 cm^{-1}. ^{1}H NMR, δ: 1.62 [m, 2 H, 4(5)-Hα], 1.80 [m, 2 H, 4(5)-Hβ], 2.00 (m, 1 H, 2-H), 2.16-2.24 [complex signal, 7 H, 1-H, 3(6)-H, 9(10)-Hβ and 9(10)-Hα]. ^{13}C NMR, δ: 24.8 [CH$_2$, C4(5)], 37.9 (CH, C1), 44.9 (CH, C2), 55.7 [C, C7(8)], 58.0 [CH$_2$, C9(10)], 63.1 [CH, C3(6)]. MS, *m/z* (%): 386 (M$^{\cdot+}$, 2), 259 (87), 217 (50), 133 (11), 132 (100). 131 (53), 117 (53), 116 (11), 115 (18), 104 (31), 91 (59), 79 (16), 78 (24), 77 (21), 67 (23), 66 (11), 65 (28), 53 (11), 51 (19). Anal. Calcd. for C$_{12}$H$_{12}$I$_2$: C, 31.12; H, 3.13, I, 65.75. Found: C, 31.15; H, 3.12, I 65.66.

Nonacyclo[13.6.6.1^{4,10}.0^{2,14}.0^{4,12}.0^{5,9}.0^{8,12}.0^{16,21}.0^{22,27}]hexacosa-2(14),16,18,20,22,24,26-heptaene[44] (**25**). A mixture of **14** (280 mg, 0.725 mmol) and 11,12-dimethylene-9,10-ethanoanthracene (**20**) (184 mg, 0.8 mmol) in anhydrous THF (10 mL) was cooled to -78 °C and a solution of *t*-butyllithium (1.7 M in pentane, 0.72 mL, 1.23 mmol) was added dropwise. After stirring for 30 min at this temperature, methanol (5 mL) and water (25 mL) were added and the mixture was extracted with diethyl ether (5 x 30 mL). The combined organic phases were dried with anhydrous Na$_2$SO$_4$ and concentrated *in vacuo* to give a residue (253 mg), which was submitted to column chromatography (silica gel, hexane/ethyl acetate in the ratio of 39:1) to give pure **25** (126 mg, 48% yield). The analytical sample was obtained by crystallization from isopropanol, m.p. 182-183 °C. IR (KBr) ν: 2939, 2870, 1455, 735 cm^{-1}. ^{1}H NMR, δ: 0.80

[m, 2 H, 6(7)-Hβ], 1.05 [m, 2 H, 6(7)-Hα] 1.10 [m, 2 H, 11(28)-Hβ], 1.50 [m, 2 H, 11(28)-Hα], 1.71 [m, 2 H, 5(8)-H], 2.10 (dt, J = 3.5 Hz, J' = 2.5 Hz, 1 H, 10-H), 2.18 (dt, J = 3.5 Hz, J' = 3.0 Hz, 1 H, 9-H), 2.34 [s, 4 H, 3(13)-H_2], 4.75 [s, 2 H, 1(15)-H], 6.91-6.94 [complex signal, 4 H, 18(19)-H and 24(25)-H], 7.22-7.27 [complex signal, 4 H, 17(20)-H and 23(26)-H]. ^{13}C NMR, δ: 21.7 [CH_2, C6(7)], 29.8 [CH_2, C3(13)], 34.2 (CH, C10), 48.5 [C, C4(12)], 51.4 (CH, C9), 52.0 [CH_2, C11(28)], 56.6 [CH, C1(15)], 58.8 [CH, C5(8)], 122.2 (CH) and 122.3 (CH) [C17(20) and C23(26)], 124.1 [CH, C18(19) and C24(25)], 142.4 [C, C2(14)], 146.3 (C) and 146.5 (C) [C16(21) and C22(27)]. MS, m/z (%): 363 ($M^{\cdot +}$ + 1, 20), 362 ($M^{\cdot +}$, 64), 295 (11), 294 (18), 293 (11), 253 (11), 252 (10), 217 (19), 216 (68), 215 (29), 204 (10), 203 (28), 202 (25), 179 (23), 178 ($[C_{14}H_{10}]^{\cdot +}$, 100), 91 (12), 67 (14). Anal. Calcd. for $C_{28}H_{26}$.1/8 isopropanol: C, 92.10; H, 7.36. Found: C, 92.16; H, 7.25.

***Syn*- and *anti*-1,11-diphenyl-18-oxaheptacyclo-[9.6.1.1^{2,8}.0^{2,10}.0^{3,7}.0^{6,10}.0^{12,17}]nonadeca-12,14,16-triene,**[44] **(16) and (19).** A mixture of **14** (60 mg, 0.16 mmol) and 1,3-diphenylisobenzofuran (50 mg, 0.18 mmol) in anhydrous THF (10 mL) was cooled to -78 °C and a solution of *t*-butyllithium (1.7 M in pentane, 0.16 mL, 0.27 mmol) was added dropwise. After stirring for 30 min at this temperature, methanol (5 mL) and water (25 mL) were added and the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated *in vacuo* to give a residue (90 mg), which was submitted to column chromatography (silica gel, hexane/ethyl acetate in the ratio 95:5) to give a mixture of **16** and **19** (59 mg) in a ratio of 1:1. On crystallization from isopropanol, a mixture of **16** and **19** partially enriched in the first one (48 mg, 77% yield) was obtained, m.p. 198-204 °C. IR (KBr) ν: 2952, 2867, 1592, 1496, 1448, 1299, 1279, 977, 918, 881, 748, 700 cm^{-1}. MS, m/z (%): 402 (19) $[M]^{\cdot +}$, 335 (27), 334 (68), 325 (10), 319 (10), 318 (22), 298 (20), 297 (76), 271 (30), 270 (55), 257 (14), 253 (11), 251 (14), 241 (26), 240 (10), 239 (23), 231 (24), 229 (38), 228 (13), 226 (11), 215 (21), 203 (11), 202 (17), 194 (10), 193 (23), 178 (10), 165 (30), 131 (10), 117 (22), 115 (14), 105 (100), 91 (31), 78 (10), 77 (60), 67 (30), 51 (10).

*NMR data of **16** obtained from the spectra of the mixture.* ^1H NMR δ: 1.16 [m, 2 H, 4(5)-Hα], 1.52 [m, 4 H, 9(19)-Hα and 9(19)-Hβ], 1.67 [m, 2 H, 4(5)-Hβ], 2.24 (m, 1 H, 8-H), 2.34 [pseudo q, J = 2.5 Hz, 2 H, 3(6)-H], 2.52 (pseudo q, J = 3.0 Hz, 1 H, 7-H), 6,92 [dd, J = 5.5 Hz, J' = 3.0, 2 H, 14(15)-H], 7.05 [dd, J = 5.5 Hz, J' = 3.0 Hz, 2 H, 13(16)-H], 7.34 (broad t, J = 7.5 Hz, 2 H, H*para*), 7.43 (pseudo t, J = 7.5 Hz, 4 H, H*meta*), 7.57 (dd, J = 7.5 Hz, J' = 1.5 Hz, 4 H, H*ortho*). ^{13}C NMR, δ: 23.5 [CH_2, C4(5)], 33.9 (CH, C8), 48.1 [CH_2, C9(19)], 54.8 [CH, C3(6)], 56.8 (CH, C7), 64.9 [C, C2(10)], 88.4 [C, C1(11)], 121.2 [CH, C14(15)], 125.6 (CH, C*ortho*), 125.9 [CH, C13(16)], 127.2 (CH, C*para*), 128.2 (CH, C*meta*), 138.6 (C, C*ipso*), 148.2 [C, C12(17)].

*NMR data of **19** obtained from the spectra of the mixture.* ^1H NMR, δ: 0.96 [m, 4 H, 4(5)-Hβ and 9(19)-Hβ], 1.16 [m, 2 H, 4(5)-Hα], 1.75 [dd, J = 8.0 Hz, J' = 2.5 Hz, 2 H, 9(19)-Hα], 2.28 [pseudo q, J = 2.5 Hz, 2 H, 3(6)-H], 2.31 (m, 1 H, 8-H), 2.42 (pseudo q, J = 3.0 Hz, 1 H, 7-H), 6,85 [dd, J = 5.5 Hz, J' = 3.0, 2 H, 14(15)-H], 7.03 [dd, J = 5.5 Hz, J' = 3.0 Hz, 2 H, 13(16)-H], 7.33 (broad t, J = 7.5 Hz, 2 H, H*para*), 7.44 (pseudo t, J = 7.5 Hz, 4 H, H*meta*), 7.61 (dd, J = 8.0 Hz, J' = 1.0 Hz, 4 H, H*ortho*). ^{13}C NMR, δ: 22.9 [CH_2, C4(5)], 38.2 (CH, C8), 47.1 [CH_2, C9(19)], 54.0 (CH, C7), 55.4 [CH, C3(6)], 65.5 [C, C2(10)], 87.5 [C, C1(11)], 119.8 [CH, C14(15)], 125.6 (CH, C*ortho*), 126.1 [CH, C13(16)], 127.2 (CH, C*para*), 128.3 (CH, C*meta*), 138.5 (C, C*ipso*), 149.5 [C, C12(17)].

***Syn*- and *anti*-2,12-dioxanonacyclo-[13.5.1.1^{3,9}.0^{1,3}.0^{4,8}.0^{7,11}.0^{11,13}.0^{13,17}.0^{16,20}]docosane,**[44] **(24) and (23).** A mixture of sodium (450 mg, 19.6 mmol) in anhydrous 1,4-dioxane (20 mL) was heated under reflux till sodium melted.

Then, **14** (740 mg, 1.92 mmol) was added at once and the mixture was heated under reflux for 4 h. The cold mixture was filtered and concentrated *in vacuo* to give an oily residue (230 mg). GC/MS analysis of this residue (conditions A) showed the presence of five main components:

21** or **22 (rt 23.5 min, 19% relative area), *m/z* (%): 265 (21), 264 (100) $[M]^{\cdot+}$, 221 (11), 207 (12), 195 (13), 193 (12), 181 (17), 169 (15), 168 (11), 167 (22), 165 (13), 155 (19), 153 (12), 143 (12), 141 (21), 131 (14), 130 (11), 129 (24), 128 (21), 117 (18), 115 (21), 105 (12), 91 (38), 79 (19), 77 (23), 67 (17).

22** or **21 (rt 23.4 min, 24% relative area), *m/z* (%): 265 (21), 264 (100) $[M]^{\cdot+}$, 196 (24), 181 (16), 169 (13), 168 (16), 167 (18), 165 (10), 155 (16), 153 (11), 143 (10), 141 (14), 131 (10), 129 (20), 128 (19), 117 (13), 115 (21), 105 (19), 95 (10), 93 (13), 91 (42), 83 (10), 81 (14), 79 (25), 78 (11), 77 (28), 69 (34), 67 (29), 65 (16), 57 (17), 55 (23), 53 (12), 51 (10).

*Dihydrodimer of **8*** (rt 17.9 min, 26% relative area), *m/z* (%): 267 (3), 266 (20) $[M]^{\cdot+}$, 237 (11), 211 (15), 200 (22), 199 (32), 198 (85), 197 (15) 183 (10), 170 (11), 169 (17), 157 (14), 156 (15), 155 (17), 145 (10), 144 (15), 143 (29), 142 (11); 141 (18), 133 (17), 132 (17), 131 (48), 130 (54), 129 (36), 128 (21), 120 (13), 119 (31), 118 (20), 117 (41), 116 (10), 115 (22), 111 (11), 109 (10), 107 (16), 106 (34), 105 (35), 104 (14), 97 (22), 96 (10), 95 (22), 93 (34), 92 (35), 91 (100), 85 (22), 83 (23), 82 (10), 81 (33), 80 (23), 79 (64), 78 (19), 77 (43), 71 (37), 70 (13), 69 (58), 68 (10), 67 (95), 66 (15), 65 (24), 57 (63), 56 (15), 55 (48), 53 (19).

*Addition product of **8** and 1,4-dioxane* (rt 12.0 min, 10% relative area), *m/z* (%): 221 (6), 220 (49) $[M]^{\cdot+}$, 162 (14), 158 (10), 153 (11), 152 (12), 151 (24), 145 (13), 135 (16), 134 (12), 133 (20), 132 (10), 131 (14), 129 (14), 120 (16), 119 (16), 117 (29), 112 (18), 108 (12), 107 (15), 106 (12), 105 (33), 104 (14), 99 (10), 96 (10), 95 (15), 94 (18), 93 (29), 92 (44), 91 (84), 87 (63), 86 (65), 81 (22), 80 (38), 79 (77), 78 (20), 77 (41), 73 (20), 68 (12), 67 (100), 66 (25), 65 (30), 59 (20), 58 (21), 55 (16), 53 (20), 51 (12).

*Dihydrodeiodination product of **14*** (rt 3.3 min, 17% relative area), *m/z* (%): 135 (1), 134 (11) $[M]^{\cdot+}$, 119 (33), 106 (16), 105 (27), 93 (31), 92 (70), 91 (55), 80 (85), 79 (70), 78 (21), 77 (30), 67 (75), 66 (100), 65 (19), 53 (11), 51 (12).

The above mixture was dissolved in CH_2Cl_2 (5 mL), cooled in an ice-water bath and treated with an excess of an acetone solution of dimethyldioxirane (DMD) (90 mL, 0.16 M, 14.4 mmol) and stirred at room temperature for 15 h. Evaporation of the solvents at reduced pressure gave an oily residue (235 mg) which was submitted to column chromatography [silica gel (40 g), hexane / ethyl acetate mixtures). On elution with an hexane / ethyl acetate mixture in the ratio of 95:5, a mixture of diepoxides **24** and **23** (40 mg, 14 % total yield) was obtained. This mixture could not be separated by crystallization from diethyl ether, hexane / ethyl acetate or chloroform. Flash column chromatography of this mixture [silica gel (13 g), hexane / ethyl acetate in the ratio of 39:1] gave a mixture of **23** and **24** (17 mg), enriched in one of them.

GC/MS analysis of this mixture (conditions C):

23** or **24 (rt 23.8 min, 30% relative area), *m/z* (%): 297 (1), 296 (5) $[M]^{\cdot+}$, 229 (19), 228 (100), 160 (16), 147 (10), 133 (16), 132 (10), 131 (31), 129 (15), 121 (12), 120 (10), 119 (14), 118 (10), 117 (53), 115 (20), 107 (20), 105 (31), 104 (19), 103 (10), 95 (10), 93 (20), 92 (18), 91 (83), 81 (10), 79 (49), 78 (22), 77 (36), 69 (19), 67 (37), 66 (16), 65 (23), 55 (28), 53 (20).

24** or **23 (rt 24.1 min, 70% relative area), *m/z* (%): 297 (1), 296 (5) $[M]^{\cdot+}$, 229 (11), 228 (24), 175 (10), 162 (16), 160 (21), 159 (17), 157 (10), 149 (12), 148 (13), 147 (13), 145 (12), 144 (11), 133 (21), 132 (14), 131

(41), 130 (11), 129 (18), 128 (10), 123 (15), 121 (19), 120 (17), 119 (20), 118 (10), 117 (55), 116 (11), 115 (21), 109 (11), 107 (17), 106 (35), 105 (38), 104 (22), 103 (12), 95 (16), 94 (14), 93 (27), 92 (21), 91 (100), 81 (13), 80 (10), 79 (62), 78 (27), 77 (44), 69 (24), 67 (49), 66 (14), 65 (27), 55 (33), 53 (24), 51 (11).

^{13}C NMR data of ***24*** *or* ***23*** *obtained from the spectra of the mixture*, δ: 24.9 [CH_2, C5(6,18,19)], 29.7 [CH, C9(15)], 39.9 [CH_2, C10(14,21,22)], 48.9 [CH, C8(16)], 50.4 [CH, C4(7,17,20)], 75.1 [C, C1(3,11,13)].

^{13}C NMR data of ***23*** *or* ***24*** *obtained from the spectra of the mixture*, δ: 27.6 [CH_2, C5(6,18,19)], 30.1 [CH, C9(15)], 43.2 [CH_2, C10(14,21,22)], 53.5 [CH, C8(16)], 53.9 [CH, C4(7,17,20)], 78.0 [C, C1(3,11,13)].

The ^{1}H NMR spectrum of the mixture consist of a complex absorption at δ 1.5-3.2 ppm.

3,3',7,7'-Tetramethyl-1,1'-bi(tricyclo[3.3.0.0^{3,7}]octyl) (29). A mixture of sodium (230 mg, 10.0 mmol) in anhydrous 1,4-dioxane (10 mL) was heated under reflux till sodium melted. Then, **31** (388 mg, 1.00 mmol) was added at once and the mixture was heated under reflux for 4 h. The cold mixture was filtered and concentrated *in vacuo* to give an oily residue (130 mg). On crystallization from pentane, diene **6**[1] (103 mg, 77% yield) was obtained. The residue from the evaporation of the mother liquors was submitted to column chromatography (silica gel, hexane) giving rise to slightly impure **29** as a waxy product (16 mg, 12% approximate yield). ^{1}H NMR (300 MHz), δ: 1.13 (s, 12 H, 4 CH_3), 1.32-1.58 (complex signal, 16 H, methylene H), 2.06 [t, J = 2.7 Hz, 4 H, 5(5')-H]; ^{13}C NMR, δ: 17.0 (CH_3, 3(3',7,7')-CH_3], 41.5 [CH, C5(5')], 47.0 [C, C3(3',7,7')], 53.8 [C, C1(1')], 54.1 [CH_2, C4(4',6,6')], 55.8 [CH_2, C2(2',8,8')]; GC/MS (conditions B, rt 9.3 min), *m/z* (%): 270 (6) $[M]^{\cdot+}$, 255 (26), 241 (16), 228 (33), 227 (26), 214 (14), 213 (29), 199 (29), 186 (10), 185 (19), 172 (13), 171 (20), 161 (12), 159 (24), 157 (32), 147 (13), 145 (21), 143 (20), 135 (142), 134 (29), 133 (21), 131 (16), 129 (12), 121 (21), 120 (16), 119 (36), 117 (12), 115 (10), 109 (21), 108 (19), 107 (58), 105 (44), 95 (100), 94 (84), 93 (69), 92 (12), 91 (51), 81 (21), 79 (55), 77 (34), 69 (15), 67 (28), 55 (34).

16,17-Dimethyloctacyclo[14.2.1.1^{14,17}.0^{1,13}.0^{2,9}.0^{3,7}.0^{6,13}.0^{8,12}]icosan-2-ol[44] (32). Sodium (3.7 g, 160 mmol) in 1,4-dioxane (25 mL) was melted in an argon atmosphere by heating the mixture under reflux. A mixture of diiodides **26** (0.55 g, 1.34 mmol) and **31** (2.60 g, 6.70 mmol) was added at once and the mixture was heated under reflux for 4 h. The mixture was allowed to cool to room temperature and filtered, washing the solid material with 1,4-dioxane (2 x 5 mL). The combined filtrate and washings were concentrated *in vacuo* and the residue (780 mg) was analyzed by GC/MS. The main components were dienes **6** (55% relative area) and **34** (16% relative area) and dihydrodimer **29** (15% relative area). Column chromatography of this mixture (silica gel, mixtures hexane / ethyl acetate) gave **6** (480 mg, 53% yield). Several fractions eluted with hexane / ethyl acetate in the ratio of 95:5 contained a minimum amount of a new compound which was characterized as **32**, while no fractions containing **34** were isolated.

Spectroscopic data of 34: Significant ^{1}H NMR data from the spectrum of the mixture (300 MHz), δ: 1.04 [s, 6 H, 16(17)-CH_3], 1.69 (broad, J = 12.3 Hz, 4 H), 3,41 (d, J = 12.3 Hz, 4 H) [15(18,19,20)-H_2], ^{13}C NMR data from the spectrum of the mixture, δ: 24.2 [CH_3, 16(17)-CH_3], 27.9 [CH_2, C4(5,10,11)], 41.0 [C, C16(17)], 46.0 [CH_2, C15(18,19,20)], 49.1 [CH, C7(8)], 54.2 [CH, C3(6,9,12)], 132.1 (C) and 135.5 (C) [C1(14) and C2(13)]. GC/MS (conditions B, rt 17.6 min), *m/z* (%): 293 (23), 292 (100) $[M]^{\cdot+}$, 277 (48), 264 (28), 263 (12), 249 (26), 237 (35), 235 (14), 225 (15), 223 (22), 221 (15), 211 (14), 209 (16), 207 (16), 198 (13), 197 (27), 196 (11), 195 (30), 193 (14), 185 (13), 184 (16), 183 (36), 182 (12), 181 (26), 179 (17), 178 (12), 172 (11), 171 (31), 170 (20), 169 (32), 168 (11), 167 (23), 166 (12), 165 (23), 159 (16), 158 (13), 157 (37), 156 (20), 155 (38), 154 (12), 153 (20), 152 (12), 145 (29), 144 (18), 143 (48), 142 (26), 141 (35), 133

(17), 132 (11), 131 (36), 130 (15), 129 (48), 128 (40), 127 (11), 121 (10), 119 (32), 118 (14), 117 (38), 116 (15), 115 (42), 107 (27), 106 (20), 105 (47), 104 (11), 103 (17), 95 (31), 94 (17), 93 (33), 92 (15), 91 (89), 89 (11), 83 (10), 81 (20), 79 (57), 78 (16), 77 (56), 67 (23), 65 (27), 57 (13), 55 (39), 53 (23), 51 (13).

Spectroscopic data of ***32***: ^{1}H NMR, δ: 0.96 [s, 6 H, 16(17)-CH_3], 1.17 [pseudo dt, J = 10.5 Hz, J' = 3.0 Hz, 2 H, 15(20)-Hα], 1.26 [dd, J = 11.0 Hz, J' = 2.5 Hz, 2 H, 18(19)-Hα], 1.50 (broad s, 1 H, OH), 1.57 [dddd, J = 14.5 Hz, J' = 11.5 Hz, J'' = 7.0 Hz, J''' = 2.5 Hz, 2 H, 4(10)-Hα], 1.70 (t, J = 3.0 Hz, 1 H, 14-H), 1.84 [ddt, J = 14.0 Hz, J' = 12.0 Hz, J'' = 6.0 Hz, 2 H, 5(11)-Hα], 1.94 [ddd, J = 14.0 Hz, J' = 8.0 Hz, J'' = 5.5 Hz, 2 H, 4(10)-Hβ], 2.03 [t, J = 5.0 Hz, 2 H, 6(12)-H], 2.13 [dd, J = 10.5 Hz, J' = 1.0 Hz, 2 H, 15(20)-Hβ], 2.22 [d, J = 10.5 Hz, 2 H, 18(19)-Hβ], 2.31 [ddd, J = 14.5 Hz, J' = 8.5 Hz, J'' = 3.0 Hz, 2 H, 5(11)-Hβ], 2.34 [m, 2 H, 7(8)-H], 2.38 [m, 2 H, 3(9)-H]. ^{13}C NMR, δ: 22.2 [CH_3, 16(17)-CH_3], 25.3 [CH_2, C4(10)], 31.8 [CH_2, C5(11)], 41.8 [C, C16(17)], 44.1 (CH, C14), 45.1 [CH_2, C18(19)], 45.8 [CH_2, C15(20)], 47.6 [CH, C7(8)], 48.5 (C, C1), 52.7 (C, C13), 58.4 [CH, C6(12)], 58.8 [CH, C3(9)], 80.6 (C, C2). GC/MS (conditions B, rt 15.8 min), *m/z* (%): 310 (6) $[M]^{\cdot +}$, 254 (23), 253 (100), 235 (39), 159 (11), 143 (10), 91 (10), 67 (12).

2,15-Dioxanonacyclo[16.2.1.1^{16,19}.0^{1,3}.0^{3,10}.0^{4,8}.0^{7,14}.0^{9,13}.0^{14,16}]docosane[44] **(35).** Sodium (4.6 g, 200 mmol) in 1,4-dioxane (75 mL) was melted in an argon atmosphere by heating the mixture under reflux. A mixture of diiodides **26** (8.24 g, 20.0 mmol) and **30** (1.44 g, 4.00 mmol) was added at once and the mixture was heated under reflux for 4 h. The mixture was allowed to cool to room temperature and filtered, washing the solid material with diethyl ether (3 x 10 mL). The combined filtrate and washings were concentrated *in vacuo* and the residue (4.08 g) was analyzed by GC/MS. The above residue was taken in CH_2Cl_2 (40 mL), the solution was cooled in an ice-bath and treated with an excess of an acetone solution of DMD (210 mL, 0.19 N, 40 mmol). After stirring for 15 h at room temperature, the solvent was eliminated at reduced pressure and the residue (3.76 g) was analyzed by GC/MS and submitted to column chromatography (silica gel, hexane / ethyl acetate mixtures). On elution with hexane / ethyl acetate in the ratio of 95:5, **35** (758 mg, 64% yield) was obtained. The analytical sample was prepared by crystallization from diethyl ether, mp 224-226 °C (dec.). IR (KBr), ν: 3066, 2966, 2926, 2894, 1477, 1412, 1311, 1104, 1040, 975, 950, 895, 848 cm^{-1}; ^{1}H NMR, δ: 1.63 [m, 4 H, 5(6,11,12)-Hα], 2.05 [dd, J = 13.0 Hz, J' = 8.0 Hz,4 H, 17(20,21,22)-Hα], 2.16 [d, J = 13.0 Hz, 4 H, 17(20,21,22)-Hβ], 2.30 [m, 4 H, 5(6,11,12)-Hβ], 2.70 [m, 2 H, 18(19)-H], 2.74 [m, 2 H, 8(9)-H], 3.00 [m, 4 H, 4(7,10,13)-H]; ^{13}C NMR, δ: 25.6 [CH_2, C5(6,11,12)], 33.9 [CH, C18(19)], 38.3 [CH_2, C17(20,21,22)], 47.5 [CH, C8(9)], 53.8 [CH, C4(7,10,13)], 73.3 (C) and 76.8 (C) [C1(16) and C3(14)]. MS, *m/z* (%): 296 (8) $[M]^{\cdot +}$, 278 (9), 239 (9), 190 (24), 169 (10), 157 (13), 145 (24), 143 (21), 141 (11), 133 (14), 131 (28), 130 (21), 129 (35), 128 (21), 123 (12), 122 (13), 121 (12), 120 (23), 119 (20), 118 (11), 117 (36), 115 (27), 108 (18), 107 (40), 106 (19), 105 (31), 104 (11), 103 (10), 96 (25), 95 (54), 94 (49), 93 (23), 92 (13), 91 (88), 83 (11), 81 (18), 80 (25), 79 (100), 78 (27), 77 (45), 69 (34), 67 (88), 66 (47), 65 (31), 55 (37), 53 (19), 51 (11). Anal. calcd. for $C_{20}H_{24}O_2$: C 81.04, H 8.16; Found: C 81.05, H 8.16.

X-ray Crystal-Structure Determination of 35.

A prismatic crystal was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined by automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-*K*α radiation, using w/2θ scan technique. 1473 reflections were measured in the range $2.91 \leq \theta \leq 29.94$. 1428 reflections were assumed as observed by applying the condition $I \geq 2\,\sigma\,(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz polarization but no absorption corrections were made. The structure was solved by Direct methods, using the SHELXS computer program[45] and refined by the full-matrix least-squares method with the

Table 10

Experimental data of the X-ray crystal structure determination of 35.

Molecular formula	$C_{20}H_{24}O_2$	F(000)	1280
Molecular mass	296.39	d(calcd) [Mg m^{-3}]	1.356
Temperature	293(2)K	Size of crystal [mm]	0.1 x 0.1 x 0.2
Crystal system	Orthorhombic	Measured reflections	1473
Space group	Pbca	Independent reflections	1473
Cell parameters [a]		Observed reflections	1744
a [Å]	8.288(2)	μ(Mo-$K\alpha$) [mm^{-1}][b]	1.481
b [Å]	13.478(9)	R	0.065
c [Å]	25.993(8)	Rw	0.125
α [°]	90	Diff. Four. $\Delta\rho_{max}$[c] (eÅ^{-3})	0.165
β [°]	90	$\Delta\rho_{min}$[d] (eÅ^{-3})	-0.159
γ [°]	90	Refined parameters	273
V [Å^3]	2904(2)	Max. shift / e.s.d.	2.9
Z	8		

[a] Determined by automatic centering of 25 reflections ($12 \leq \theta \leq 21°$).

[b] μ(Mo-$K\alpha$), Linear absorption coefficient. Radiation Mo-$K\alpha$ (λ = 0.71069Å).

[c] Maximum and [d] minimum peaks in final difference synthesis.

SHELX-93 computer program[46] using 1473 reflections (very negative intensities were not assumed). The function minimized was Σ w $[|F_o|^2 - |F_c|^2]^2$, where w = $[\sigma^2(I) + (0.0143P)^2 + 20.742P]^{-1}$, and P = $(|F_o|^2 + 2 |F_c|^2) / 3$. f, f' and f'' were taken from International Tables of X-ray Crystallography.[47] The extinction coefficient was 0.0000 (1). All H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. Goodness of fit on F^2 = 0.829 for all observed reflections. Mean shift / e.s.d. = 0.01.

18,19-Dimethyl-2,15-dioxanonacyclo[16.2.1.1^{16,19}.0^{1,3}.0^{3,10}.0^{4,8}.0^{7,14}.0^{9,13}.0^{14,16}]docosane[44] **(36).** A similar procedure to that described for **35** was followed, except for the use of a ratio **26**/**31** of 4:1. Starting from **26** (2.47 g, 5.99 mmol) and **31** (0.58 g, 1.50 mmol), a mixture (1.22 g) was obtained which was reacted with DMD to give a new mixture (1.0 g) which on column chromatography gave **35** (286 mg, 59 % yield). Crystallized from diethyl ether showed m.p. 168-170 °C (dec.). IR (KBr): ν = 3055, 2938, 2892, 1472, 1418, 1258, 1162, 1092, 978, 899, 836 cm^{-1}; ^{1}H NMR, δ: 1.17 [s, 6 H, 18(19)-CH_3], 1.63 [m, 4 H, 5(6,11,12)-Hα], 1.92 (d, J = 12.5 Hz, 4 H) and 2.28 (d, J = 12.5 Hz, 4 H) [17(20,21,22)-Hα and -Hβ], 2.30 [m, 4 H, 5(6,11,12)-Hβ], 2.73 [m, 2 H, 8(9)-H], 2.99 [m, 4 H, 4(7,10,13)-H]; ^{13}C NMR, δ: 24.5 [CH_3, 18(19)-CH_3], 25.6 [CH_2, C5(6,11,12)], 42.9 [C, C18(19)], 47.1 [CH_2, C17(20,21,22)], 47.5 [CH, C8(9)], 53.8 [CH, C4(7,10,13)], 73.8 (C) and 74.6 (C) [C1(16) and C3(14)]. MS, m/z (%): 324 (4) $[M]^{\cdot +}$, 268 (14), 267 (10), 202 (18), 190 (18), 173 (10), 157 (11), 147 (10), 146 (10), 145 (18), 143 (13), 135 (47), 134 (15), 133 (14), 131 (16), 130 (20), 129 (27), 128 (17), 123 (15), 121 (18), 120 (16), 119 (59), 118 (11), 117 (34), 115 (23), 110 (18), 109 (16), 108 (19), 107 (68), 106 (21), 105 (42), 96 (15), 95 (96), 94 (92), 93 (54), 92 (24), 91 (82), 81 (19), 80 (19), 79 (100), 78 (15), 77 (45), 69 (16), 68 (12), 67 (82), 66 (12), 65 (25), 55 (44), 53 (20). Anal. calcd. for $C_{22}H_{28}O_2$: C 81.43, H 8.70; Found: C 81.40, H 8.69.

Acknowledgements

We are indebted to Prof. Dr. F. J. Luque for helpful suggestions about the computational part of this work. We thank the *Serveis Científico-Tècnics* of the University of Barcelona and particularly Dr. *M. Feliz* and Dr. *A. Linares* for recording the NMR spectra, Dr. *A. Marín* for MS spectra and the *Centre de Supercomputació de Catalunya* for computational facilities. We also thank Ms. *P. Domenech* from the *Centro de Investigación y Desarrollo* (C.I.D.) (Barcelona, Spain) for carrying out the elemental analyses. Grant 1997SGR 00140 from the Comissionat per a Universitats i Recerca (Generalitat de Catalunya) is gratefully acknowledged.

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