CYCLOHEPTATRIENE DIMERS: NEW PRECURSORS OF DIAMANTANE

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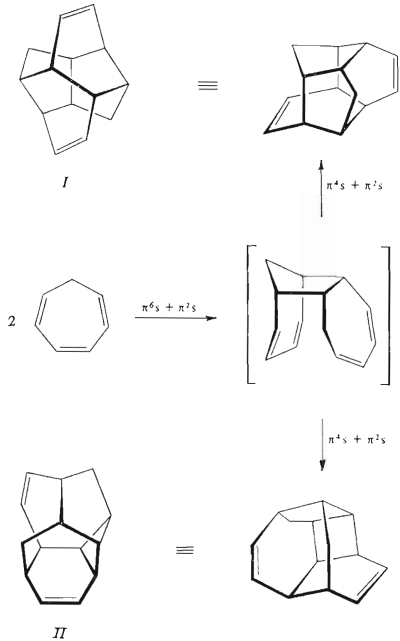
Dimerization of cycloheptatriene, catalyzed by titanium complexes, afforded pentacyclo-[$8.4.0.0^{3,7}.0^{4,14}.0^{6,11}$]tetradeca-8,12-diene (*I*) (10%) and pentacyclo[$7.5.0.0^{2,8}.0^{5,14}.0^{7,11}$]-tetradeca-3,12-diene (*II*) (90%). Structure of both dimers and their derivatives was determined by means of ^{1}H-NMR, ^{13}C-NMR and mass spectra. On heating, the diene *II* was converted into the more stable isomer *I*. On hydrogenation and further catalytic isomerization, both *I* and *II* gave diamantane in high yield.

Recently[1] we reported on the catalyzed dimerization of cycloheptatriene (CHT). The $(C_2H_5)_2AlCl$–$TiCl_4$ catalyst has been shown to induce dimerization of cycloheptatriene *via* consecutive $[_\pi 6_s + _\pi 2_s]$ and $[_\pi 4_s + _\pi 2_s]$ cycloadditions, furnishing two novel cage-like hydrocarbons: pentacyclo[$8.4.0.0^{3,7}.0^{4,14}.0^{6,11}$]tetradeca-8,12-diene (*I*) and pentacyclo[$7.5.0.0^{2,8}.0^{5,14}.0^{7,11}$]tetradeca-3,12-diene (*II*) (Scheme 1). This paper deals with the structure elucidation of *I* and *II* and some aspects of their chemistry.

The structure of *I* was derived from its IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra. The mass spectrum of *I* displayed molecular ion $C_{14}H_{16}$, *m/z* 184, and abundant fragments *m/z* 92 (the base peak of the spectrum) and *m/z* 91. The presence of the $C_7H_8^{+\bullet}$ base peak indicates[2] that *I* is formed from cycloheptatriene by a cycloaddition sequence, *i.e.* that the catalyzed dimerization is not accompanied by hydrogen transfers or carbon–carbon bond rearrangements. The infrared spectrum of *I* showed one $\nu(C{=}C)$ band at 1625 cm^{-1}. The ^{13}C-NMR spectrum exhibited only seven carbon signals, indicating that the molecule of *I* must possess a symmetry element (center, twofold axis or plane not bisecting the skeletal carbon atoms). ^{13}C-Chemical shifts and off-resonance multiplicities further revealed that *I* is a pentacyclic diene with disubstituted double bonds, two equivalent methylenes and four pairs of magnetically equivalent sp^3 methines. This implies that all the fourteen carbon atoms must be built into the pentacyclic skeleton. With these data at hand, we generated[3] all



SCHEME 1

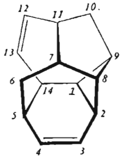
possible pentacyclic C_{14} dienes whose structures did not contradict the spectral data. Subsequent selections were made using the ^{1}H-NMR spectrum. All eight kinds of protons in *I* were well resolved at 200 MHz. The vinylic protons appeared as doublets of doublets of doublets ($H_{(1)}$: $\delta = 6{\cdot}05$ ddd, $J = 8{\cdot}8$, $6{\cdot}3$ and $1{\cdot}2$ Hz; $H_{(2)}$: $\delta = 5{\cdot}86$ ddd, $J = 8{\cdot}8$, $7{\cdot}2$ and $0{\cdot}6$ Hz). The coupling constant $J_{1,2} = 8{\cdot}8$ Hz indicates that the double bonds in *I* are situated in six-membered or larger rings, in agreement with its infrared spectrum. Double resonance experiments enabled the assignment of allylic protons: $H_{(3)}$ (multiplet, $\delta = 2{\cdot}58$) and $H_{(4)}$ (multiplet, $\delta = 1{\cdot}96$). The vicinal ($J_{1,4}$, $J_{2,3}$) and allylic ($J_{1,3}$, $J_{2,4}$) coupling constants provided evidence that both allylic protons lie near the plane of the double bond. The multiplet of $H_{(3)}$ was further affected by irradiating the remaining two methines at $\delta = 2{\cdot}23$ and $\delta = 1{\cdot}79$. On the other hand, $H_{(4)}$ is apparently coupled to the methine at $\delta = 1{\cdot}79$

($H_{(6)}$) only. From the symmetry properties of the system it follows that the allylic positions cannot be bridged by any single methine group bearing the $H_{(6)}$ proton. Unavoidably this means that $H_{(3)}$ is in fact coupled to the symmetry image of $H_{(6)}$, *i.e.* to $H_{(6')}$. Of the two methylene protons, one appears as a doublet ($H_{(7)}$: $\delta = 1{\cdot}27$, $J_{7,8} = 10{\cdot}8$ Hz) and the other as a doublet of doublets of doublets ($H_{(8)}$: $\delta = 1{\cdot}11$, $J = 10{\cdot}8$, $3{\cdot}9$ and $3{\cdot}3$ Hz). Decoupling experiments proved that $H_{(7)}$ has only a geminal coupling while $H_{(8)}$ is also coupled to $H_{(5)}$ and $H_{(6)}$. This implies that the methylene group is placed between two methines in such a way that the torsion angles $H_{(7)}$—C—C—$H_{(6)}$ and $H_{(7)}$—C—C—$H_{(5)}$ are close to ninety degrees.

Inspection of the list of more than 850 generated structures revealed that only the structure *I* met the requirements imposed by all the spectral data. The structural assignment was further supported by the vicinal ^{13}C—^{1}H coupling constants (^{3}J). Hereinafter the numbering of carbon atoms in *I* is chosen to conform with the proton numbering. Both $C_{(1)}$ and $C_{(2)}$ show only two non-zero vicinal ^{3}J coupling. Since there are three hydrogen atoms vicinal to $C_{(1)}$ (*i.e.* $H_{(3)}$, $H_{(6)}$ and $H_{(4')}$) and $C_{(2)}$ ($H_{(4)}$, $H_{(5)}$ and $H_{(6')}$), one of the coupling constants must be very small. Indeed, molecular models show that the corresponding torsion angles $C_{(1)}$—$C_{(4)}$—$C_{(6)}$—$H_{(6)}$ and $C_{(2)}$—$C_{(3)}$—$C_{(5)}$—$H_{(5)}$ approach ninety degrees which means that $^{3}J \rightarrow 0$. Similarly, the methylene carbon $C_{(7)}$ appears as a doublet of doublets (disregarding the direct coupling) because of zero coupling constants with $H_{(3')}$ and $H_{(5')}$. The ^{3}J couplings observed are caused by the $H_{(3)}$ and $H_{(4)}$ protons. The allylic carbon atoms $C_{(3)}$ and $C_{(4)}$ are coupled to several protons. From their complex multiplets it could be deduced that there is at least one large ^{3}J coupling constant for each allylic carbon. All these data agree well with the proposed structure of *I*. The complete assignment of all protons and carbons in *I* is depicted in Fig. 1.

On hydrogenation, *I* afforded the saturated derivative *Ia*. The coupling pattern of the former $H_{(7)}$ and $H_{(8)}$ protons in the ^{1}H-NMR spectrum of *Ia* resembles closely that of *I*. However, the $H_{(7)}$ doublet in *Ia* is shifted 0·54 ppm downfield with respect to *I*. This effect can be understood if we consider the spatial arrangements of protons on the pentacyclic framework. Molecular models show that in *I* the $H_{(7)}$ proton lies within the shielding cone of the double bond[4]. In the saturated hydrocarbon *Ia*, this effect is absent and, in turn, the $H_{(7)}$ proton is deshielded[5] by van der Waals interactions with the exo $H_{(1)}$ and $H_{(2)}$ protons. The chemical shifts of $H_{(8)}$ changes only little on passing from *I* to *Ia*. Epoxidation of *I* gave the diepoxide *Ib* as the sole product. Since *Ib* preserves the C_2 symmetry of the skeleton, the epoxidation of both double bonds must have proceeded from the equivalent sides of the pentacyclic molecule. The stereochemical assignment of the oxirane rings follows from the ^{1}H-NMR spectrum of *Ib*. In addition to the expected vicinal coupling constants of the oxirane protons ($J = 4{\cdot}2$ and $3{\cdot}8$ Hz), there is a further downfield shift of the well recognizable $H_{(7)}$ doublet appearing now at $\delta = 2{\cdot}00$ ppm. Inspection of models reveals that $H_{(7)}$ falls into the deshielding region of the oxirane ring. The stereospecific formation of *Ib* corresponds to approach of the reagent from the less hindered side of the skeleton.

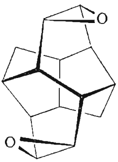
The main product of the dimerization, *II*, proved to be a more difficult task. The mass spectrum of *II* displays molecular ion $C_{14}H_{16}$, m/z 184 and abundant fragments m/z 92 (the base peak of the spectrum) and m/z 91. The molecular ion of *II* is substantially less abundant than that of the symmetrical isomer *I*. In the infrared spectrum, *II* exhibited two ν(C=C) bands at 1 623 and 1 653 cm^{-1}. The ^{13}C-NMR spectrum of *II* shows all fourteen carbon atoms. Off-resonance multiplicities confirmed that *II* contains four different olefin methines, two methylenes and eight sp^3 methines. Hence, *II* is a pentacyclic C_{14} diene lacking any symmetry element. In the 200 MHz ^1H-NMR spectrum of *II*, all four vinylic protons are resolved. The vicinal coupling constants confirm that both double bonds are located in six-membered or larger rings. Of four allylic proton signals ($H_{(2)}$, $H_{(5)}$, $H_{(11)}$ and $H_{(14)}$), $H_{(2)}$ is shifted downfield, while the others overlap with other three skeletal protons ($H_{(1)}$, $H_{(8)}$ and $H_{(9)}$). The considerable downfield shift of $H_{(1)}$, $H_{(2)}$, $H_{(8)}$ and $H_{(9)}$ indicates the presence of a tetrasubstituted cyclobutane ring[6]. The vicinal coupling constants of $H_{(2)}$ allow for two structures, *i.e.* *II*, or another one with the



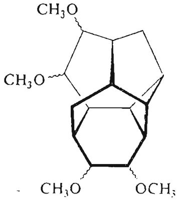
II

III

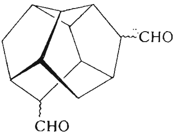
reversed arrangement of the cyclobutane and cyclopentane rings (*III*). Inspection of relaxed Dreiding models shows that both *II* and *III* have very similar torsion angles between all involved skeletal protons. Hence, even the knowledge of all coupling constants would not permit any unambiguous structural assignment to the asymmetrical dimer. Fortunately, the problem was solved by means of chemical correlation. We found that *II* was isomerized quantitatively to *I* when heated above 150°C.This enables to distinguish between the structures *II* and *III*. As shown in Scheme 1, the formation of both *I* and *II* from cycloheptatriene can be visualized as a sequence of $[_\pi 6_s + {}_\pi 2_s]$ and $[_\pi 4_s + {}_\pi 2_s]$ cycloadditions. The first step is symmetry forbidden in the ground state[7] and it proceeds only in the presence of a catalyst[1]. The second steps are symmetry allowed, so that *I* and *II* can be interconverted *via* a common intermediate[1]. On the other hand, the formation of *III* could be depicted in two different ways, either as a $[_\pi 4_s + {}_\pi 2_s]$, $[_\pi 2_s + {}_\pi 2_s]$ or a $[_\pi 2_s + {}_\pi 2_s]$, $[_\pi 4_s + {}_\pi 2_s]$ cycloaddition sequence. Clearly, *I* and *III* have no common intermediate, total decomposition to two cycloheptatriene molecules being symmetry forbidden in both cases. We have also attempted another chemical correlation. Double ring contraction in *II* by reaction with thallium(III) nitrate[8] was expected to yield the dialdehyde *IV* which, after removal of the aldehyde groups, would furnish a new hydrocarbon *V* with C_2 symmetry. Unfortunately, the reaction of *II* with thallium(III) nitrate led to a mixture of tetramethoxy derivatives *IIj*. Since the ring contraction was observed neither with *I* nor with *II*, we concluded that, in contrast to the monocyclic series[8], this reaction is not reliable with strained polycyclic olefins.



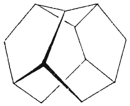
Ib



IIj



IV



V

Hydrogenation of *II* proceeded smoothly to the first stage but complete hydrogenation to the saturated compound *IIa* was rather sluggish. Epoxidation of *II* with one equivalent of *m*-chloroperoxybenzoic acid can be stopped at the first

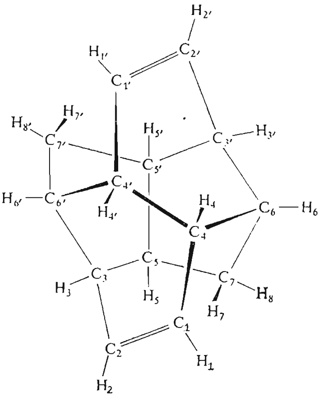
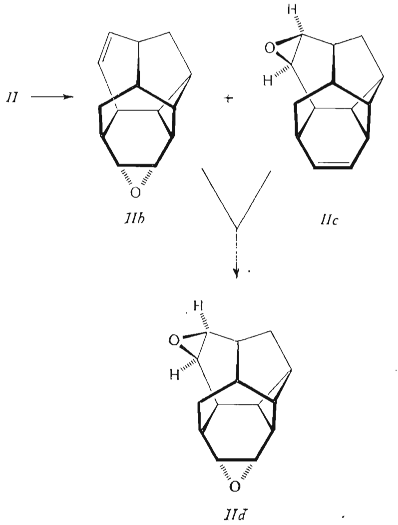


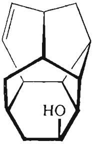
FIG. 1

Numbering of Protons and Carbons in the Diene *I* stage. However, the product was a mixture of two monoepoxides *IIb* (90%) and *IIc* (10%). Prolonged epoxidation with a large excess of the reagent yielded the single diepoxide *IId*. The orientation of the oxirane rings in *IIb,c,d* was established by means of their ^{1}H-NMR spectra. Although the signals of the oxirane protons in the spectrum of *IIb* overlapped with those of other skeletal methines, they were resolved by means of the lanthanide-induced shift. Upon addition of the Eu(fod)$_3$ reagent, the oxirane protons appeared as doublets of doublets at $\delta = 4{\cdot}62$ ($J = 4{\cdot}4$ and $4{\cdot}4$ Hz) and $\delta = 5{\cdot}04$ ($J = 6{\cdot}6$ and $4{\cdot}4$ Hz). These data indicate the *endo*-configuration of the oxirane ring in *IIb*. Moreover, the $H_{(6)}$ proton doublet is shifted downfield to $\delta = 2{\cdot}03$ ppm due to the effect of the *endo*-oriented oxirane ring. The multiplets of oxirane protons in *IId* overlap considerably. Inspection of models shows that the epoxidation of the 12,13-double bond from either side would produce isomers undiscernible by ^{1}H-NMR spectra. The downfield shift of the second methylene doublet ($H_{(10)}$, $\delta = 2{\cdot}73$) cannot be used for stereochemical assignment because the same deshielding effect could be expected for both orientations of the oxirane ring. Tentatively, we suggest the configuration depicted in Scheme 2, since it corresponds to the reagent approach from the less hindered side of the skeleton.

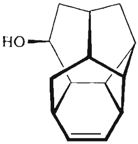


SCHEME 2

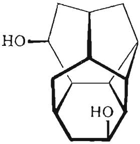
Hydroboration of *II* can be conducted to produce either a mixture of two unsaturated alcohols *IIe* (80%) and *IIf* (20%) or, after prolonged reaction time, a mixture of two diols *IIg* (80%) and *IIh* (20%). The position and configuration of the hydroxyl group in *IIe* follow from the ^{1}H-NMR spectrum. The vicinal coupling constants of the CH—O proton ($\delta = 3{\cdot}89$ dd, $J = 6{\cdot}3$ and $4{\cdot}8$ Hz) are consistent with both 3-*exo* and 4-*endo* hydroxyl configurations. Double resonance experiments proved that the smaller coupling constant corresponds to the $H_{(2)}$—$H_{(3)}$ coupling which supports the assumed structure of *IIe*. The identity of the protons vicinal to the hydroxyl group was established by converting *IIe in situ* to the corresponding trichloroacetylcarbamate (TAI method[9]). Both the trichloroacetylcarbamate and acetate *IIi* exhibited similar acylation effects. The $C_{(6)}$ methylene doublet is shifted upfield with respect to the parent alcohol *IIe*. This provides an additional evidence[9] for the 3-*exo* configuration of the hydroxyl group in *IIe*.



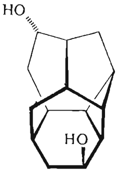
IIe



IIf



IIg



IIh

The alcohol *IIf* arises by hydroboration of the 12,13-double bond as corroborated by the distinct proton signal at $C_{(2)}$; this proton is coupled to the olefinic protons. Vicinal coupling constants of the CH—O proton agree with the hydroxyl at $C_{(12)}$ as well as at $C_{(13)}$. To solve this problem, we converted *IIf in situ* to the corresponding trichloroacetylcarbamate. In this way the isomeric alcohols can be distinguished due to a different orientation of the acyl function with respect to the $H_{(10)}$ proton ($\delta = 2{\cdot}15$ d, $J = 13{\cdot}3$ Hz). The trichloroacetylcarbamate-induced shift of the latter proton is very small and downfield, in line with other remote skeletal protons. This strongly suggests that the $H_{(10)}$ proton and the hydroxyl group are situated on the reverse sides of the cycloheptane ring. Together with the vicinal coupling constants this allows for both positional and stereochemical assignment in *IIf*. The positions and configurations of the hydroxyl groups in diols *IIg* and *IIh* were determined using the vicinal coupling constants and acylation effects in the same manner as in the case of *IIe* and *IIf*.

The different course of epoxidation and hydroboration of the 3,4-double bond in *II* is rather peculiar. Nevertheless, it can be understood if we consider the nature of reagents and accessibilities of $C_{(3)}$ and $C_{(4)}$ from the *exo*- and *endo*-sides of the skeleton. Thus, the simultaneous attack of both $C_{(3)}$ and $C_{(4)}$ during epoxidation proceeds from the less hindered *endo*-side, since the *exo*-side of $C_{(4)}$ is hindered by the asymmetrically situated $C_{(6)}$ methylene group. On the other hand, the $C_{(3)}$ center alone appears to be more easily accessible from the *exo*-side which explains the preferential formation of the 3-*exo*-alcohol *IIe* during the hydroboration. It should be noted that both double bonds in *II* do not react with mercuric acetate and 9-borabicyclo(3.3.1)nonane.

The saturated hydrocarbons *Ia* and *IIa* belong to the family of diamantane isomers[10]. The easy accessibility of both compounds from cheap starting chemicals prompted us to investigate their isomerization. Indeed, both *Ia* and *IIa* on treatment with aluminium chloride in dichloromethane[11] afforded diamantane in an excellent yield. The melting point, ^{1}H-NMR, ^{13}C-NMR and mass spectra of diamantane prepared in this way were identical with the literature data[12–14]. The most convenient route from cycloheptatriene to diamantane comprises the catalyzed dimerization followed by isomerization of *II* to *I*. The second step circumvents the rather tedious hydrogenation of *II* and causes no loss of material because the isomerization is nearly quantitative. The hydrogenation of *I* is rapid and leaves no partially unsaturated products. Consequently, the isomerization of *Ia* to diamantane is clean, producing only a very small amount of polymers. The present preparation of diamantane represents an alternative to the well-known Binor-S route[11].

EXPERIMENTAL

The melting points were determined on a Boetius hot stage apparatus in sealed evacuated capillaries. Mass spectra were recorded on a JEOL JMS D-100 spectrometer at 75 eV, using either a direct inlet or the gas chromatograph — mass spectrometer coupling. ^{1}H-NMR spectra were measured on a Varian XL-200 instrument (200·05 MHz, FT-mode) in deuteriochloroform with tetramethylsilane as an internal standard. Chemical shifts are expressed in the δ (ppm) scale. ^{13}C-NMR spectra were measured on a JEOL FX-60 spectrometer (15·036 MHz, FT-mode) in deuteriochloroform at 25°C. Apparent coupling constants were obtained by first-order analysis. Infrared spectra were recorded on a Zeiss (Jena) IR-75 grating spectrometer in potassium bromide pellets. The expression "worked up" means that the solution was dried over sodium sulfate, filtered and the solvents were evaporated on a rotatory evaporator.

Dimerization of Cycloheptatriene

Diethylaluminium chloride (2 mmol in 1 ml of benzene) and titanium(IV)chloride (0·1 mmol in 1 ml of benzene) were successively added under argon to cycloheptatriene (10 ml). After 6 h standing at 40°C the unreacted cycloheptatriene was distilled off, the residue dissolved in hexane and chromatographed on a silica gel column (elution with light petroleum), yielding 0·3 g of *I* and 2·9 g of *II*. The unreacted cycloheptatriene (60%) was recycled without further purification. The conversion depended mainly on the purity of the starting cycloheptatriene. It is advisable to use only colourless, carefully purified material that does not contain reducible impurities. The conversion in one cycle can be raised up to 60% by doubling the amount of catalyst. *I* and *II* were further purified by crystallization from methanol or by sublimation *in vacuo*. I: m.p. 219 to 221°C. For $C_{14}H_{16}$ (184·3) calculated: 91·25% C; 8·75% H; found: 91·39% C; 8·86% H. IR spectrum, cm^{-1}: 3032, 2960, 2930, 2857, 1625, 1450, 1380, 1370, 1327, 1303, 1280, 1259, 1217, 1185, 1150, 1053, 1047, 997, 970, 880, 840, 830, 813, 797, 760, 748, 713, 677, 580, 547; mass spectrum: *m/z* (rel. intensity): 184 (30·5), 142 (13·2), 129 (11·4), 117 (13·4), 115 (10·9), 106 (15), 93 (29·5), 92 (100), 91 (74); ^{1}H-NMR spectrum: 1·11 ddd (J = 10·8, 3·9, 3·3 Hz) 2 H, 1·27 d (J = 10·8 Hz) 2 H, 1·79 m 2 H, 1·96 m 2 H, 2·23 m 2 H, 2·58 m 2 H, 5·86 ddd (J = 8·8, 7·2, 0·6 Hz) 2 H, 6·05 ddd (J = 8·8, 6·3, 1·2 Hz) 2 H; ^{13}C-NMR spectrum: 132·3 ddd (J = 161·1, 4·9, 4·9 Hz) $C_{(1)}$, 129·0 ddd (J = 161·1, 4·9, 4·9 Hz; $C_{(2)}$, 43·40 ddt (J = 128·2, 8·5 Hz) $C_{(3)}$, 40·10 dm (J = 139·9 Hz) $C_{(5)}$, 38·70 ddt (J = 131·8, 10·3 Hz) $C_{(4)}$, 36·1 dm $C_{(6)}$, 31·6 tdd (J = 129·4, 4·9, 3·7 Hz) $C_{(7)}$. *II*: m.p. 217—225°C (decomposition). For $C_{14}H_{16}$ (184·3) calculated: 91·25% C; 8·75% H; found: 91·44% C; 8·60% H. IR spectrum, cm^{-1}: 3057, 3013, 2947, 2913, 2853, 1653, 1623, 1446, 1436, 1393, 1341, 1330, 1293, 1283, 1267, 1243, 1233, 1222, 1193, 1180, 1159, 1123, 1085, 1053, 1031, 1005, 985, 947, 900, 875, 829, 827, 814, 794, 783, 767, 743, 711, 700, 682, 670, 617, 477; mass spectrum: *m/z* (rel. intensity): 184 (8·8), 142 (7·9), 129 (8), 117 (10·8), 106 (8·4), 93 (23), 92 (100), 91 (78·7); ^{1}H-NMR spectrum: 1·62—1·78 m 2 H, 1·85 to 1·98 m 2 H, 2·51 m 1 H, 2·70—2·93 m 6 H, 3·19 dq (J_d = 8·2 Hz) 1 H, 5·24 ddd (J = 10·6, 8·6 0·6 Hz) 1 H 5·50 dd (J = 11·0 9·0 Hz) 1 H, 6·01 dd (J = 11·0, 9·0 Hz) 1 H, 6·22 dd (J = 10·6 8·8 Hz) 1 H; ^{13}C-NMR spectrum: 139·6 d, 133·5 d, 128·3 d, 127·8 d, 53·3 d, 50·2 d, 45·0 d, 44·7 d, 40·6 d, 40·3 d, 40·2 d, 39·6 d, 35·2 t, 31·5 t.

Isomerization of *II* to *I*

The diene *II* (2 g) was heated in a sealed tube at 150°C/13 Pa for 12 h. The semi-crystalline product was purified by sublimation *in vacuo* to yield 1·95 g (97%) of *I*, identical in all respects with the product of dimerization of cycloheptatriene (*vide supra*).

Pentacyclo[8.4.0.0^{3,7}.0^{4,14}.0^{6,11}]tetradecane (*Ia*)

The diene *I* (2 g) was hydrogenated over platinum (150 mg) in ethanol (50 ml) at 40°C for 4 h. The catalyst was filtered off, the solvent evaporated and the residue sublimed (140°C/13 Pa) to yield 1·85 g (90%) of *Ia*, m.p. 253—255°C. For $C_{14}H_{20}$ (188·3) calculated: 89·30% C, 10·70% H; found: 89·11% C, 10·53% H. Mass spectrum: *m/z* (rel. intensity): 188 (100), 159 (18·8), 145 (17·3), 132 (9·1), 131 (15·1), 117 (19·7), 106 (12·7), 93 (16·7), 92 (22·1), 91 (29·7), 79 (25·7). ^{1}H-NMR spectrum: 1·27 ddd (J = 12·1, 4·4 Hz) 2 H, 1·44 m 2 H, 1·58 m 4 H, 1·71 m 2 H, 1·77 m 2 H, 1·81 d (J = 12·1 Hz) 2 H, 1·89 m 2 H, 2·03 m 2 H, 2·30 m 2 H ^{13}C-NMR spectrum: 46·86 d, 41·83 d, 41·50 d, 34·44 d, 32·49 t, 26·07 t, 22·01 t.

8,9:12,13-Diepoxypentacyclo[8.4.0.0^{3,7}.0^{4,14}.0^{6,11}]tetradecane (*Ib*)

A solution of the diene *I* (500 mg, 2·7 mmol) in dichloromethane (20 ml) was treated with *m*-chloroperoxybenzoic acid (1·3 g, 7·5 mmol) at 0°C for 12 h. The mixture was diluted with ether (20 ml), washed with water and sodium carbonate and then worked up. The crude diepoxide *Ib* was purified by crystallization from pentane to yield 510 mg (87%) of pure product, m.p. 330 to 331°C. For $C_{14}H_{16}O_2$ (216·3) calculated: 77·75% C, 7·46% H; found: 77·52% C, 7·24% H. Mass spectrum: *m/z* (rel. intensity): 216 (10·8), 187 (17·9), 169 (16·7), 159 (23), 131 (32), 129 (34·6), 111 (32), 107 (39·2), 91 (100), 81 (43·6), 79 (91), 77 (53·1), ^{1}H-NMR spectrum: 1·20 ddd (J = = 12·8, 3·7, 3·2 Hz) 2 H, 2·00 d (J = 12·8 Hz) 2 H, 2·39 m 4 H, 2·45 m 2 H, 2·64 m 2 H, 3·13 dd (J = 4·5, 4·2 Hz) 2 H, 3·19 dd (J = 4·5, 3·8 Hz) 2 H; ^{13}C-NMR spectrum: 52·1 d, 51·8 d, 45·5 d, 42·2 d, 39·6 d, 31·0 d, 30·1 t.

Pentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradecane (*IIa*)

The diene *II* (1·5 g) was hydrogenated over platinum (150 mg) in a mixture of ethanol (50 ml) and dioxane (20 ml) at 40° for 12 h. The catalyst was filtered off, the solvents were evaporated and the residue purified by sublimation *in vacuo* to yield 1·35 g (88%) of *IIa*, m.p. 314—315°C. For $C_{14}H_{20}$(188·3) calculated: 89·30% C, 10·70% H; found: 89·48% C, 10·61% H. Mass spectrum: m/z (rel. intensity): 188 (37·4), 173 (20), 160 (20·9), 159 (22·6), 145 (31·3), 131 (38·3), 117 (24·4), 105 (27·8), 93 (52·2), 91 (89·6), 79 (100). ^{1}H-NMR spectrum: 2·86 m 2 H, 2·55, 2·48 m 5 H, 1·92 d (J = 13·0 Hz) 1 H, 1·78 m 6 H, 1·72 d (J = 14·0 Hz) 1 H, 1·67 m 3 H, 1·25 m 2 H; ^{13}C-NMR spectrum: 51·36 d, 51·00 d, 43·17 d, 43·04 d, 41·42 d, 41·06 d, 35·90 d, 35·82 d, 31·35 t, 25·46 t, 25·14 t (2 C), 24·20 t, 23·96 t.

3,4-Epoxypentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradecane (*IIb*)

A solution of the diene *II* (200 mg) and *m*-chloroperoxybenzoic acid (200 mg) in dichloromethane (10 ml) was kept at 0°C for 12 h. The mixture was worked up as described for *Ib* and the product was purified by column chromatography (silica gel, light petroleum–ether, 2 : 1) affording 180 mg (77%) of *IIb*, m.p. 317—320°C (decomposition). For $C_{14}H_{16}O$ (200·3) calculated: 84·00% C, 8·05% H; found: 84·23% C, 8·15% H. Mass spectrum: m/z (rel. intensity): 200 (30·4), 172 (13), 171 (11), 129 (50·4), 117 (34·8), 115 (34·8), 105 (32·6), 92 (47·8), 91 (100), 79 (70·9), 77 (58·3). ^{1}H-NMR spectrum: 5·92 m 1 H, 5·68 m 1 H, 3·22 m, 3·07, 2·92 m 8 H, 2·37 m 2 H, 2·03 d (J = 12·5 Hz) 1 H, 1·63 m 3 H; after addition of Eu(fod)$_3$: 6·28 dd (J = 10·7, 8·6 Hz) 1 H, 5·97 dd (J = 10·7, 9·8 Hz) 1 H, 5·04 dd (J = 6·6, 4·4 Hz) 1 H, 4·62 dd (J = 4·4, 4·4 Hz) 1 H, 4·03 m 2 H, 3·78 m 2 H, 3·32 m 2 H, 3·23 m 2 H, 2·78 m 2 H, 3·55 d (J = 12·5 Hz) 1 H, 2·19 m 2 H, 1·92 m 1 H. The minor component *IIc* (lower R_F value) was not obtained in the pure form. ^{1}H-NMR spectrum: 5·92 dd (J = 9·4, 6·1 Hz), 5·27 dd (J = 12·3, 5·6 Hz).

3,4:12,13-Diepoxypentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradecane (*IId*)

A mixture of monoepoxides *IIb* and *IIc* (100 mg) in dichloromethane (10 ml) was treated with *m*-chloroperoxybenzoic acid (150 mg) at 20°C for 72 h. The reaction mixture was worked up as described for *Ib* and the product (a single spot in thin layer chromatography) was recrystallized from a chloroform–pentane mixture. Yield 90 mg (83%); m.p. 318—321°C (decomposition). For $C_{14}H_{16}O_2$ (216·3) calculated: 77·75% C, 7·46% H; found: 77·40% C, 7·50% H. Mass spectrum: m/z (rel. intensity): 216 (1·4), 198 (1·4), 197 (2·2), 187 (5·4), 169 (8·9), 159 (8·6), 155 (8·3), 129 (31), 117 (42·5), 107 (38), 91 (100), 81 (42·4), 79 (89·2), 77 (52·5). ^{1}H-NMR spectrum: 3·56 m, 3·50 m 2 H, 3·23 m, 3·10 m 6 H, 2·75 d (J = 13·0 Hz) 1 H, 2·68 m, 2·57 m 2 H, 2·15 d (J = 13·0 Hz) 1 H, 1·75 m 2 H, 1·65 m, 1·23 m 2 H. ^{13}C-NMR spectrum: 57·8, 57·4, 57·3, 54·7, 50·4, 50·1, 42·3, 41·2, 40·9, 37·9, 34·5, 31·3, 29·2, 28·8.

Reaction of *II* with Thallium(III) Nitrate

Thallium(III) nitrate (2·1 g) was added to a solution of *II* (400 mg) in methanol (20 ml) and 1,2-dimethoxyethane (10 ml) and the mixture was stirred at 25°C for 24 h. The precipitate was filtered off, washed with ether and the solvents were evaporated. The residue was purified by chromatography on a silica gel column (elution with ether) to yield 350 mg (60%) of the oily product *IIj*. For $C_{18}H_{28}O_4$ (308·4) calculated: 70·10% C, 9·15% H; found: 70·35% C, 8·83% H. Mass spectrum m/z (rel. intensity): 308 (0·2), 276 (1·8), 230 (2·5), 246 (1·8), 214 (1·8), 200 (4·3), 172(3·2), 91 (15·4), 45 (100).

Hydroboration of *II*

A solution of the diene *II* (500 mg) in tetrahydrofuran (10 ml) was added at 0°C under argon to a solution of borane–tetrahydrofuran complex (prepared from 200 mg of sodium borohydride and 550 mg of boron trifluoride etherate). The mixture was stirred at 0°C for 12 h, hydrolyzed with methanol and treated with 3M-NaOH and hydrogen peroxide. The usual work-up afforded a mixture which was separated on a silica gel column (elution with ether–light petroleum) to yield as the first fraction 3-*exo*-hydroxypentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradec-12-ene (*IIe*), (240 mg), m.p. 275—280°C (decomposition). For $C_{14}H_{18}O$ (202·2) calculated: 83·12% C, 8·97% H; found: 82·90% C, 9·17% H. Mass spectrum: *m/z* (rel. intensity): 202 (34·4), 184 (14·3), 173 (7·4), 169 (15·1), 159 (9·7), 129 (35·1), 117 (50·6), 91 (100), 79 (57·1), 77 (38·3). ^{1}H-NMR spectrum: 5·78 dd (J = 11·0 Hz) 1 H, 5·73 dd (J = 11·5, 11·0 Hz) 1 H, 3·89 dd (J = 6·3, 4·8 Hz) 1 H, 3·06 m 1 H, 2·86 m, 2·75 m 4 H, 2·58, 2·46 2 H, 2·28 d (J = 12·8 Hz) 1 H, 2·16 dd (J = 14·7, 6·3 Hz) 1 H, 1·89 m 2 H, 1·63 m 4 H. Trichloroacetylcarbamate, ^{1}H-NMR spectrum: 5·85 dd (J = 11·0 Hz) 1 H, 5·80 dd (J = 11·5, 11·0 Hz) 1 H, 5·10 dd (J = 6·3, 4·8 Hz) 1 H, 3·18 m 1 H, 2·89 m, 2·75 m 4 H, 2·61, 2·48 m 2 H, 2·27 dd (J = 14·7, 6·3 Hz) 1 H, 2·21 d (J = 12·8 Hz) 1 H, 1·94 m 1 H, 1·77 dd (J = 14·7, 6·8 Hz) 1 H, 1·65 m 3 H. Acetate (*IIi*), m.p. 83—85°C; ^{1}H-NMR spectrum: 5·53 dd (J = 10·8, 10·0 Hz), 5·52 dd (J = 10·8, 10·4 Hz) 1 H, 5·00 dd (J = = 6·6, 5·0 Hz) 1 H, 2·97 m 1 H, 2·88 m 1 H, 2·75 m 1 H, 2·59 m 1 H, 2·47 m 1 H, 2·20 dd (J = 16·4, 6·4 Hz) 1 H, 2·18 d (J = 13·2 Hz) 1 H, 2·02 s 3 H, 1·90 m 1 H, 1·63 m 1 H, 1·58 m 1 H.

Further elution afforded 13-hydroxypentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradec-3-ene (*IIf*), (60 mg), m.p. 293—295°C. For $C_{14}H_{18}O$ (202·2) calculated: 83·12% C, 8·97% H; found: 83·45% C, 8·78% H. Mass spectrum: *m/z* (rel. intensity): 202 (14·9), 184 (12·8), 169 (11·5), 143 (14·9), 129 (26·3), 117 (37·2), 96 (41·9), 91 (100), 79 (58·8). ^{1}H-NMR spectrum: 5·79 m 2 H, 4·55 ddd (J = = 8·9, 7·1, 1·8 Hz) 1 H, 2·98 m 2 H, 2·78 m, 2·64 m 4 H, 2·47 dd (J = 5·8, 5·7 Hz) 1 H, 2·42 dd (J = 5·9, 5·8 Hz) 1 H, 2·15 d (J = 13·3 Hz) 1 H, 2·01 m 1 H, 1·86 dd (J = 8·8, 6·0 Hz) 1 H, 1·79 dd (J = 8·0, 4·9 Hz) 1 H, 1·73 d (J = 12·0 Hz) 1 H, 1·65 dd (J = 5·6, 3·8 Hz) 1 H, 1·59 dd (J = 8·8, 3·4 Hz) 1 H. Trichloroacetylcarbamate, ^{1}H-NMR spectrum: 5·87 m, 5·70 ddd, 3·05 m, 2·83 m, 2·80 m, 2·64 m, 2·51 dd, 2·45 dd, 2·18 d, 2·07 m, 1·91 dd, 1·86 dd, 1·75 d, 1·78 m.

Further elution with ether afforded two diols: Pentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradecane-3,12-diol (*IIh*), (40 mg), m.p. 340—345°C. For $C_{14}H_{20}O_2$ (220·3) calculated: 76·33% C, 9·15% H; found: 76·59% C, 8·97% H. Mass spectrum: *m/z* (rel. intensity): 220 (3·3), 202 (13·8), 187 (6·6), 186 (7·8), 184 (9·2), 174 (9·2), 173 (11·2), 169 (12·5), 129 (34·2), 117 (50), 105 (38·2), 91 (100), 79 (86·8). ^{1}H-NMR spectrum: 4·29 ddd (J = 9·4, 2·2, 2·2 Hz) 1 H, 4·04 ddd (J = 5·5, 5·2, 1·2 Hz) 1 H, 3·12 ddd (J = 10·8, 10·6, 5·2 Hz) 1 H, 3·03 m 1 H, 2·81 m, 2·72 m 5 H, 2·48 1 H, 2·38 d (J = 13·2 Hz) 1 H, 2·35 d (J = 13·6 Hz) 1 H, 2·24 ddd (J = 17·0, 9·4, 3·0 Hz) 1 H, 2·07 d (J = = 5·9 Hz) 1 H, 1·99 dd (J = 16·6, 5·5 Hz) 1 H, 1·87 m 2 H, 1·82 dd (J = 16·6, 5·7 Hz) 1 H, 1·66 m 1 H, 1·57 m 1 H. Pentacyclo[7.5.0.0^{2,8}.0^{5,14}.0^{7,11}]tetradecane-3,13-diol (*IIg*) (200 mg), m.p. 353—355°C. For $C_{14}H_{20}O_2$ (220·3) calculated: 76·33% C, 9·15% H; found: 76·41% C, 9·44% H. Mass spectrum: *m/z* (rel. intensity): 220 (1·5), 202 (22·4), 187 (9·9), 184 (11·3), 174 (9·9), 173 (13·4), 169 (11·7), 159 (17·7), 145 (27·5), 129 (29·6), 117 (47·9), 108 (49·3), 91 (100), 79 (84·5). ^{1}H-NMR spectrum: 4·18 ddd (J = 9·6, 6·8, 2·8 Hz) 1 H, 4·10 ddd (J = 5·1, 5·1, 1·2 Hz) 1 H, 3·14 m 2 H, 2·82 m 1 H, 2·70 m 3 H, 2·54 m 1 H, 2·39 d (J = 13·2 Hz) 1 H, 2·38 m 2 H, 2·08 m 2 H, 1·99 d (J = 13·6 Hz) 1 H, 1·95 m 2 H, 1·85 m 2 H, 1·68 ddd (J = 12·6, 3·2 Hz) 1 H. Diacetate m.p. 156—158°C, ^{1}H-NMR spectrum: 5·20 dd (J = 6·5, 3·0 Hz) 1 H, 5·16 dd (J = 5·8, 2·2 Hz) 1 H, 3·17 m 1 H, 3·04 dd (J = 15·2, 8·0 Hz) 1 H, 2·69 m 3 H, 2·53 m 3 H, 2·39 dd (J = 10·4, 2·8 Hz) 1 H, 2·26 d (J = 13·2 Hz) 1 H, 2·06 dd (J = 6·0 Hz) 1 H, 2·02 s 3 H, 2·00 s 3 H, 1·87 m 4 H, 1·66 ddd (J = 12·8, 5·9, 5·9 Hz) 1 H.

Isomerization of *Ia* to Diamantane

The compound *Ia* (1 g) was added to a solution of aluminum chloride (150 mg) in dichloromethane (20 ml) and the mixture was refluxed under argon for 12 h. After cooling, chloroform was added, the solution was washed successively with hydrochloric acid, water and potassium carbonate solution and then worked up. Sublimation *in vacuo* afforded 890 mg (89%) of pure diamantane, m.p. 243—245°C (ref.[11] gives 245°C, ref.[12] reports 237°C). ^{1}H-NMR spectrum: 1·69—1·71 m; ^{13}C-NMR spectrum: 38·3 t, 37·6 d, 25·9 d. The same results were obtained with *IIa* as a starting compound.

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