Tetrahedron Vol. 35, pp. 1463 to 1467
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0040-4020/79/0601-1463/$02.00/0

# STRUCTURES OF THE TRICYCLODODECENES PREPARED BY THE CATALYTICAL INTRAMOLECULAR CYCLISATION OF 1,5,9-CYCLODODECATRIENE

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(*Received in UK 14 December 1978*)

**Abstract**—The internal cyclisation of 1,5,9-cyclododecatriene, induced by a catalytical amount of $Cp_2TiCl_2$–LAH$\delta$, leads to a mixture of *cis,anti,cis*-tricyclo[7.3.0.0$^{2,6}$]-7-dodecene (1), *cis,syn,trans*-tricyclo[7.3.0.0$^{2,6}$]-7-dodecene (2), *trans,syn*-tricyclo[7.3.0.0$^{2,6}$]-6-dodecene (3) and 5,6,7,8,9,10-hexahydrobenzocyclooctene (4). The structures of the main products were determined from the spectra of a number of derivatives taking into account symmetry properties and configurational flexibility.

The $Cp_2TiCl_2$–LAH system in ether was reported to bring about the hydroalumination and isomerisation of olefins.[1,2] Recently we have found[3] that $Cp_2TiCl_2$ could be reduced by LAH in some cycloolefins at elevated temperatures and $\mu$-($\eta^5$:$\eta^5$-fulvalene)-di-$\mu$-chloro-bis(cyclopentadienyltitanium), $\mu$-($\eta^5$:$\eta^5$-fulvalene)-$\mu$-chloro-$\mu$-hydrido-bis(cyclopentadienyltitanium) and $\mu$-($\eta^5$:$\eta^5$-fulvalene)-di-$\mu$-hydrido-bis(cyclopentadienyltitanium) were the final organometallic products.[3] When the reduction was carried out in *cis,trans,trans*-1,5,9-cyclododecatriene (CDT) at its b.p., a quantitative isomerisation of CDT occurred.[4] The tricyclododecenes 1, 2 and 3 were found to be the major products accompanied by benzocyclooctene 4 (Scheme 1). The cyclisation of CDT enables an easy access to tricyclo[7.3.0.0$^{2,6}$]dodecane or *as*-indacene derivatives, because CDT can be prepared easily by the cyclotrimerisation of 1,3-butadiene.[5,6] This paper deals with the structure elucidation of 1, 2, 3 and 4; also chemistry of the tricyclo[7.3.0.0$^{2,6}$]dodecane derivatives is reported in some detail.

*Structure determination of* 1, 2, 3 *and* 4. The molecular ion of 1 appears at *m/e* 162 $(C_{12}H_{18})^{+\cdot}$ indicating four ring-plus-double-bond equivalents, the same amount as in CDT. From the IR spectrum of 1 (1649, 727 cm$^{-1}$), the presence of a double bond in a 6-membered or larger ring could be inferred. The $^1$H NMR spectrum contains a broad multiplet at 1.12–2.10 ppm, a broad triplet at 2.38 ppm (J = 7.5 Hz) and a doublet of doublets at 5.45 ppm (J = 1.4 and 0.25 Hz). The intensity ratio of these signals is 7:1:1. The $^{13}$C NMR spectrum consists of six signals (23.5t, 30.3t, 32.2t, 36.5d, 40.0d and 129.9d). It follows from the above data, that 1 is a symmetric tricyclic olefin containing one disubstituted double bond and four bridgehead methines of which two are in the allylic position to the double bond. The symmetry element is either a plane or a two-fold axis of symmetry. On ozonolysis, 1 furnished the symmetric dialdehyde **1b** (Scheme 2). The $^1$H NMR spectrum of **1b** shows only one doublet at 9.80 ppm (J = 3.9 Hz), the $^{13}$C NMR spectrum displays six signals at $\delta$(C) = 23.9t, 26.1t, 32.2t, 46.5d, 53.1d and 204.8d. The main fragmentation path in the mass spectrum of **1b**, $M^{+\cdot}(C_{12}H_{16}O_2$, *m/e* 194)$\rightarrow C_6H_9O^+$(*m/e* 97)$\rightarrow C_5H_7^+$(*m/e* 67), is compatible with the proposed structure only, if taking into account all possible dialdehydes that could have been formed. From the structure of the dialdehyde **1b**, the tricyclo[7.3.0.0$^{2,6}$]-7-dodecene skeleton could be assigned to 1 unambigously. This was confirmed by a correlation with standards: on hydrogenation (or hydroboration/hydrolysis) 1 afforded **1a** which was identical (according to GC and GC–MS) with one component of the authentical mixture of tricyclo[7.3.0.0$^{2,6}$]dodecanes prepared by Landa and Vaněk.[7]

Expoxidation of 1 gave only one epoxide **1c** according to GC and GC–MS analyses ($M^{+\cdot}$, *m/e* 178). **1c** lacks any symmetry element giving twelve signals in its $^{13}$C NMR spectrum. The acid-catalyzed opening of the epoxide ring led to the diol **1d** which was again symmetric (six signals in the $^{13}$C NMR spectrum). Based on symmetry considerations, there are four possible structures for a symmetric tricyclo[7.3.0.0$^{2,6}$]-7-dodecene: *cis,syn,cis*, *trans,syn,trans*, *cis,anti,cis* and *trans,anti,trans*. The formation of the unsymmetric epoxide **1c** indicates

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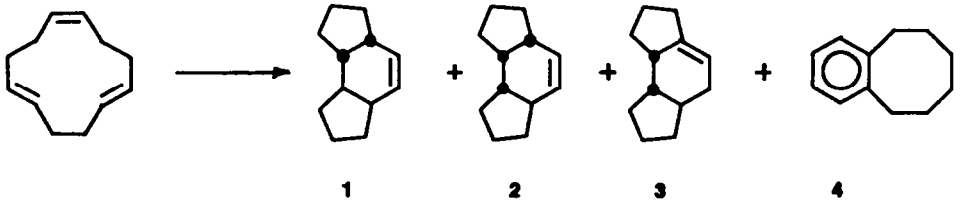
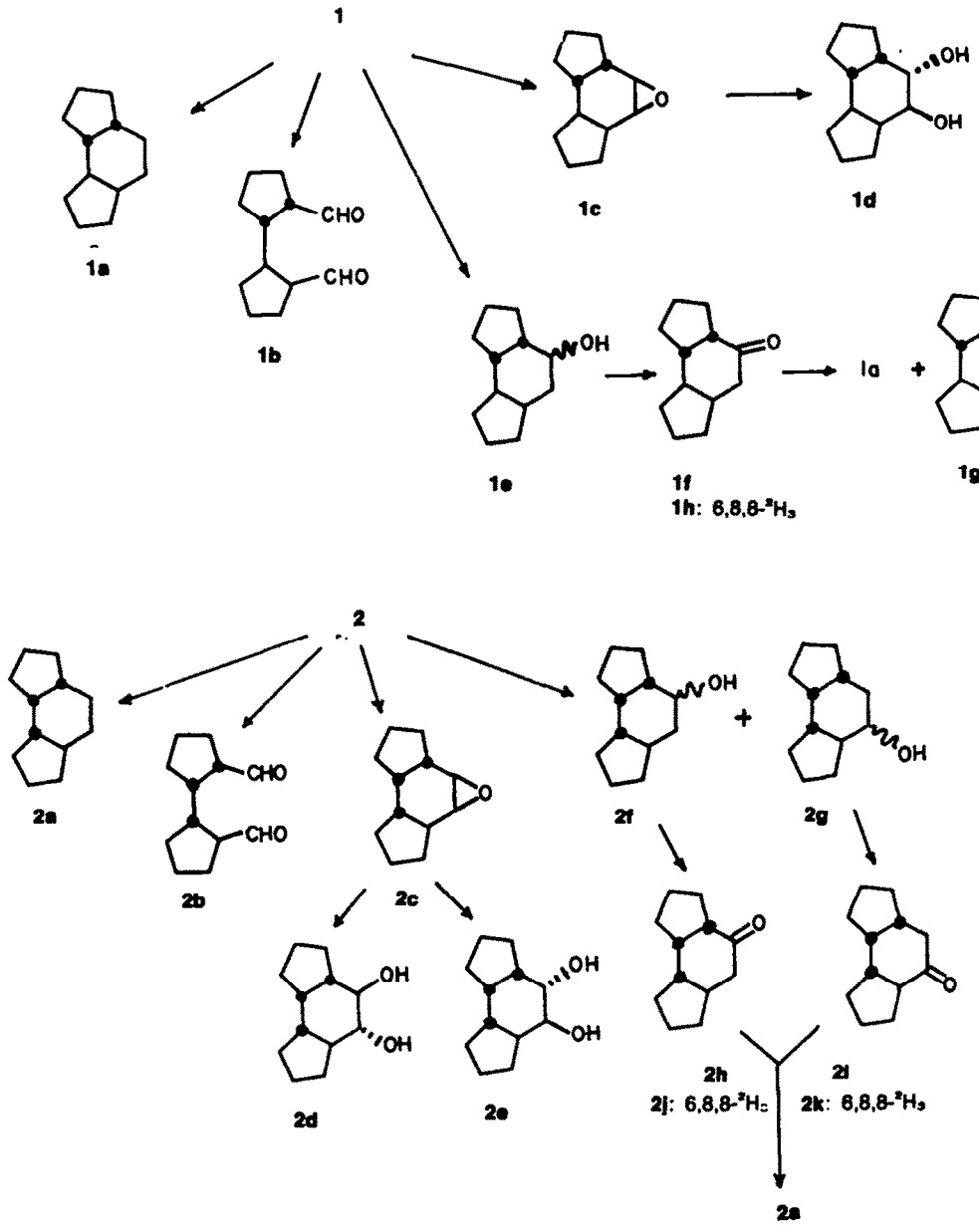



Scheme 1.




Scheme 2.

that the symmetrical compounds **1**, **1b** and **1d** belong to the $C_2$-symmetry group. This is compatible only with the *anti*-arrangement of rings. The diol **1d** shows an intramolecular hydrogen bridge in its IR spectrum ($\Delta\nu$(OH = 39 cm$^{-1}$). As **1d** is symmetric, any anomalous opening of the epoxide ring can be excluded and **1d** must be a diequatorial diol. The $^1$H NMR spectrum confirms this conclusion: since **1d** is symmetrical, both oxymethine protons are magnetically equivalent and their mutual coupling does not manifest itself in the spectrum. The coupling observed (4.4 Hz) is therefore vicinal and it corresponds to an axial-equatorial arrangement of protons on C-7 and C-9 and/or C-6 and C-8. As the opening of an epoxide leads predominantly to a diaxial diol,[8] **1** should have a flexible skeleton enabling the conversion to the diequatorial form. This is consistent only with the *cis,anti,cis* arrangement of rings in **1**. Returning to the interpretation of the $^1$H NMR spectrum of **1**, further support for the *cis,anti,cis* system could be obtained. Owing to the symmetry, both olefinic protons are magnetically equivalent and their mutual coupling does not appear in the spectrum. Of the two splittings observed, one is vicinal and the other is allylic. The double resonance experiment proved that the allylic protons at 2.38 ppm are responsible for the larger coupling. The observed magnitude of the allylic coupling implies a torsion angle about 40° thus indicating a skew position of the C-6—C-8 and/or C-7—C-9 protons.

The compound **2** shows molecular ions $C_{12}H_{18}^{+\cdot}$ (*m/e* 162) in its mass spectrum. The $^1$H NMR spectrum of **2** exhibits (in addition to the overlapping multiplets of aliphatic protons) a doublet of doublets of doublets (J = 10.3, 2.9 and 1.2 Hz) at 5.50 ppm and a doublet of doublets (J = 10.3 and 0.7 Hz) and 5.82 ppm. The $^{13}$C NMR spectrum

of 2 contains all twelve signals (22.4t, 25.2t, 25.3t, 27.9t, 29.7t, 33.4t, 37.4d, 39.7d, 41.1d, 46.4d, 129.5d and 133.1d). Thus, 2 is an unsymmetrical tricyclic olefin containing one disubstituted double bond in the 6-membered ring. This is consistent with the IR spectrum of 2 (1633 $cm^{-1}$). On ozonolysis of 2, the dialdehyde 2b was obtained, the mass spectrum of the latter being very similar to that of 1b. Hence, the tricyclo[7.3.0.$0^{2,6}$]-7-dodecene skeleton could be assigned to 2. The $^{13}C$ NMR spectrum of 2b contains twelve signals and when comparing the spectra of 2b and 1b, one analogous aldehyde group and five corresponding carbon signals can be found ($\delta$(C) within the range of 1 ppm and the same degree of protonation). However, the preserved methines (formerly C-1 and C-2) differ for 1b and 2b. On hydrogenation (or hydroboration/hydrolysis) 2 gave the tricyclic hydrocarbon 2a which was identical with another component of the authentical mixture.[7] Unsymmetrical nature of 2 allows for the *cis,syn,trans* or *cis,anti,trans* arrangement of the tricyclic skeleton. This is consistent with the $^1H$ NMR spectrum of 2 where only one allylic coupling was the same as in 1. The epoxidation of 2 afforded one unsymmetrical epoxide 2e (twelve signals in the $^{13}C$ NMR spectrum). On acid-catalysed hydrolysis of 2e, two diols were obtained: the diequatorial isomer 2d ($\Delta\nu$(OH) = 36 $cm^{-1}$) and the diaxial isomer 2e (only the free OH vibration observed at 3631 $cm^{-1}$).

As these findings have not been decisive, the final assignment of the ring annulation in 2 was based on the correlation with 1. 1 was converted to the ketone 1f which was reduced according to Huang-Minlon to a mixture of two tricyclododecanes: the major component (80%) was identical with 1a. The monor component 1g (20%), which resulted from the isomerisation on C-6, was identical with another component of the Landa's mixture.[7] In a similar manner, 2 afforded a mixture of ketones 2h and 2i (3:1). The single tricyclododecane 2a (95% according to the GC and GC/MS analyses) was obtained by the Huang-Minlon reduction of both 2h and 2i. Hence it follows that 2 has the skeleton, non-convertible to an *anti*-arranged one by a mere isomerisation on C-6 and/or C-9. As the isomerisation during the Huang-Minlon reduction need not be complete, we attempted a correlation of the ketones 1f, 2h and 2i. The degree of the isomerisation on C-6 and C-9 was checked conveniently by insertion of D atoms. Despite the high degree of exchange (1h: 90.2% $d_3$; 2j: 92.8% $d_3$; 2k: 92.5% $d_3$) achieved, no common product was obtained from 1f and 2h or 2i. Instead, only the deuteroanalogues 1h, 2j and 2k were produced suggesting that the original skeletons are more stable than those which could be formed by isomerisation on C-6 or C-9. It follows from the absence of a correlation between 1 and 2 that 2 has the *syn*-arrangement of rings. Hence, 2 is the *cis,syn,trans* isomer.

The third product 3 exhibits the molecular ion $C_{12}H_{18}^{+\cdot}$ (*m/e* 162). There is only one olefinic proton ($\delta$(H) = 5.39d ppm, J = 5.4 Hz) in the $^1H$ NMR spectrum of 3 and one quaternary $sp^2$ carbon ($\delta$(C) = 146.8s) with one methine $sp^2$ carbon ($\delta$(C) = 117.2d) in the $^{13}C$ NMR spectrum. Therefore, 3 contains a trisubstituted double bond in accordance with the IR spectrum (1673, 818 $cm^{-1}$). Both hydrogenation and hydroboration/hydrolysis of 3 yielded the hydrocarbon which was identical (according to GC and GC/MS) with 2a. Thus, 3 has the tricyclo[7.3.0.$0^{2,6}$]dodecene skeleton. The position of the double bond in 3 was determined after a conversion to the ketone 3a. The latter compound contained the keto group in the 6-membered ring ($\nu$(C=O) = 1700 $cm^{-1}$; $\delta$(C) = 213.2s). Moreover, 3a was identical with 2h according to IR, $^1H$ NMR, $^{13}C$ NMR, mass spectra and retention parameters. The correlation of 3 with 2 shows that both compounds have the same *syn*-arrangement of rings. As hydrogenation and hydroboration are known[9] to proceed from the less-hindered side of the skeleton, 3 must have the *trans,syn* configuration. The alternative *cis,syn*-annulated compound would give *cis,syn,cis* isomer in controversy with our observation (Fig. 1).

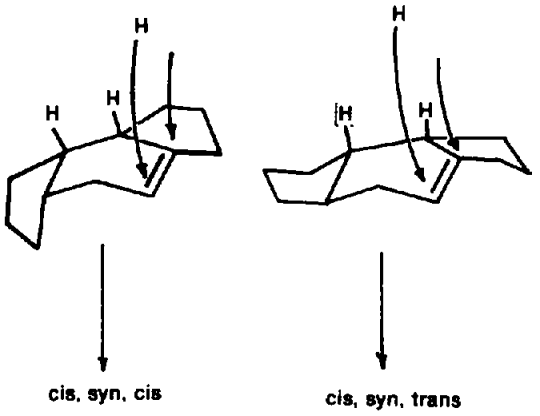



Fig. 1. The stereochemical course of hydrogenation of 3.

The structure of 4 followed directly from its spectra. The 1700–2000 $cm^{-1}$ region in the IR spectrum of 4 showed a pattern typical for an ortho-disubstituted benzene. The mass spectrum of 4 exhibits the molecular ion $C_{12}H_{16}^{+\cdot}$ (*m/e* 160) and abundant ions $C_8H_8^{+\cdot}$ (*m/e* 104). From these data it follows that 4 is 5,6,7,8,9,10-hexahydrobenzocyclooctene.

## EXPERIMENTAL

*Chemicals.* CDT (Fluka) was distilled *in vacuo* from dimeric titanocene. $Cp_2TiCl_2$ (Schuchardt) and LAH (Metallgesellschaft AG) were used without purification.

M.ps (uncorrected) were determined on a Kofler block. IR spectra were taken on a UR-75 Zeiss (Jena) grating spectrometer. The 3000–3700 $cm^{-1}$ region was monitored on a Pye-Unicam SP-700 apparatus at $3 \times 10^{-3}$ M concentrations. The $^1H$ and $^{13}C$ NMR spectra were measured on a JEOL FX-60 spectrometer (59.797 and 15.036 MHz) in $CDCl_3$ solutions with internal TMS standard at 25°. The chemical shifts (±0.01 ppm and 0.06 ppm) were calculated from the digitally obtained address differences. Mass spectra were measured on a JEOL JMS D-100 spectrometer at 75 eV by using either a direct inlet system or the GC/MS mode (columns: *A*, SE-30, 3% on Chromosorb W, 2 m, 3 mm i.d.; *B*, Stirling MTFF graphitized carbon, 2 m, 3 mm i.d.). The GC analyses were carried out on a CHROM 4 (Laboratory Instruments, Prague) gas chromatograph using the columns described above. The term "usual work-up" means that the extract was dried over $Na_2SO_4$ and the solvent was evaporated *in vacuo*.

*Cyclisation of CDT.* A mixture of $Cp_2TiCl_2$ (0.5 g, 2 mmol), LAH (0.3 g, 8 mmol) and CDT (180 ml) was magnetically stirred in a bulb sealed to the vacuum-argon line. On heating, the reduction of $Cp_2TiCl_2$ was accompanied by hydrogen evolution and by colour changes from yellow-orange to green-brown and dark brown. At 200° the exothermic cyclisation started bringing the mixture to boil and simultaneously an intense purple-red colour appeared indicating the formation of $\mu$-($\eta^5$:$\eta^5$-fulvalene)-di-$\mu$-chloro-bis(cyclopentadienyltitanium). The subsequent colour changes to dark green and bright green evidenced the formation of $\mu$-chloro-$\mu$-hydrido and di-$\mu$-hydrido titanium

complexes, respectively.[3,4] After about 10 min the cyclisation went to completion and the products were distilled off *in vacuo*. The separation on a $AgNO_3$-silica gel column (elution with cyclohexane, cyclohexane-benzene) yielded 1 (33%), 4 (16%), 3 (2%) and 2 (27%) together with a mixture of $C_{12}H_{20}$ hydrocarbons (*ca* 15%). No CDT was found in the product mixture.

*Compound* 1. Found: C, 88.70; H, 11.09. Calc. for $C_{12}H_{18}$: C, 88.82; H, 11.18%; $n_D^{20} = 1.5132$; IR(film): 1649, 1470, 1446, 1321, 1150, 935, 900, 860, 727 $cm^{-1}$; MS(*m/e*): 162, 147, 134, 133, 119, 91(base peak); $^1H$ NMR: 1.12–2.10mt (14H), 2.38 broad t (7.5 Hz, 2H), 5.45 dd (1.4 and 0.25 Hz); $^{13}C$ NMR: 129.9d, 40.0d, 36.5d, 32.2t, 30.3t, 23.5t.

*Compound* 2. Found: C, 88.68; H, 11.21. Calc. for $C_{12}H_{18}$: C, 88.82; H, 11.18%; $n_D^{20} = 1.5105$; IR(film): 1633, 1467, 1455, 1385, 1370, 1264, 1080, 965, 908, 712 $cm^{-1}$; MS(*m/e*): 162, 147, 134, 133(base peak), 119, 94, 91; $^1H$ NMR: 0.82–98mt (16H): 2.61 and 2.31 mt; 5.50ddd (10.3, 2.9 and 1.2 Hz, 1H); 5.82dd (10.3 and 0.7 Hz, 1H); $^{13}C$ NMR: 133.1d, 129.5d, 46.4d, 41.1d, 39.7d, 37.4d, 33.4t, 29.7t, 27.9t, 25.3t, 25.2t, 22.4t.

*Compound* 3. Found: C, 88.79; H, 11.33. Calc. for $C_{12}H_{18}$: C, 88.82; H, 11.18%; $n_D^{20} = 1.5122$; IR(film): 1673, 1466, 1454, 1365, 1295, 1285, 1030, 1006, 818 $cm^{-1}$; MS(*m/e*): 162, 134, 133, 119, 91, 80(base peak); $^1H$ NMR: 0.89–2.83mt (17H), 5.39d (5.4 Hz, 1H); $^{13}C$ NMR: 146.8s, 117.2d, 45.0d, 42.4d, 39.2d, 31.8t, 30.0t, 29.5t, 27.7t, 26.2t, 22.7t, 21.2t.

*Compound* 4. IR(film): 1937, 1903, 1870, 1853, 1827, 1794, 1600, 1494, 755, 713; MS(*m/e*): 160, 145, 131, 117, 104(base peak), 91.

cis,anti,cis-*Tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 1a. 1 (100 mg) was hydrogenated with Pt (5 mg) in EtOH (3 ml). The work-up and distillation (115°/1.6 kPa, bath temp.) afforded 95 mg (95%) of 1a in a 95% purity (column *A*, 100°; *B*, 180°). Found: C, 87.72; H, 12.05. Calc. for $C_{12}H_{20}$: C, 87.72; H, 12.28%; MS(*m/e*): 164, $C_{12}H_{20}^{+\cdot}$.

cis,syn,trans-*Tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 2a. Hydrogenation of 2 (100 mg) and 3 (100 mg), carried out as for 1, afforded 90 mg (90%) of 2a in a 95% purity, (column *A*, 100°; *B*, 180°). Found: C, 87.55; H, 12.15. Calc. for $C_{12}H_{20}$: C, 87.72; H, 12.27%. MS(*m/e*): 164, $C_{12}H_{20}^{+\cdot}$.

*Ozonolysis of* 1. Ozonised air was bubbled through a stirred soln of 1 (200 mg) in $CH_2Cl_2$ (5 ml) at −78° for 5 hr. Zn dust (1 g) and AcOH (2 ml) were added and the mixture was refluxed for 1 hr. Then ether (20 ml) was added, insoluble salts were filtered off and the ethereal soln was worked-up as usual. The crude 1b was identified without further purification. MS(*m/e*): 194, 176, 165, 148, 147, 97, 67(base peak); $^1H$ NMR: 1.06–2.84mt, 9.80d (J = 3.9 Hz, 2H); $^{13}C$ NMR: 204.8d, 53.1d, 46.5d, 32.2t, 26.1t, 23.9t.

*Ozonolysis of* 2. 2 (300 mg) was ozonised as described for 1 to yield 200 mg of the crude 2b. MS(*m/e*): 194, 176, 165, 148, 147, 97, 67(base peak); $^1H$ NMR: 1.16–2.87mt, 9.58d (J = 2.9 Hz, 1H), 9.79d (J = 3.9 Hz, 1H); $^{13}C$ NMR: 204.7d, 203.6d, 58.5d, 53.9d, 51.2d, 42.6d, 33.0t, 30.0t, 30.4t, 27.4t, 25.9t, 25.5t, 24.0t.

7,8 - *Epoxy* - cis,anti,cis - *tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 1c. 1 (500 mg) was treated with *m*-chloroperoxybenzoic acid (700 mg) in $CH_2Cl_2$ (5 ml) at 0° for 18 hr. The mixture was diluted with pentane, *m*-chlorobenzoic acid was filtered off and the pentane soln was worked-up. Distillation (150°/2 kPa, bath temp.) afforded 500 mg (91%) of 1c which was of a 95% purity (column *A*, 130°). Found: C, 81.05; H, 10.03. Calc. for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. MS(*m/e*): 178, 177, 160, 149, 137, 135, 131, 107, 81, 79(*base peak*), 67; $^1H$ *NMR*: 1.02–2.40mt, 3.11d (J = 4.6 Hz, 1H), 3.20t (J = 4.6 Hz), IH); $^{13}C$ NMR: 56.5d, 54.7d, 39.8d, 38.5d, 36.4d(2C), 31.5t, 30.3t, 28.5t, 27.1t, 24.0t, 22.7t.

7,8-*Epoxy*-cis,syn,trans-*tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 2c. 2c was prepared from 2 in a 90% yield as described for 1c. Found: C, 80.80; H, 10.10. Calc. for $C_{12}H_{18}O$: C, 80.85; 10.18. MS(*m/e*): 178, 177, 163, 160, 149, 135, 134, 131, 107, 95, 81, 79, 67(base peak); $^1H$ NMR: 0.93–1.87mt, 2.03mt, 2.48mt, 2.85, 3.20 (*AB*, J = 3.9 Hz); $^{13}C$ NMR: 57.2d, 54.7d, 39.1d, 37.9d, 37.0d, 36.6d, 31.3t, 27.7t, 27.1t, 26.6t, 26.2t, 21.4t.

7,8-*Dihydroxy*-cis,anti,cis-*tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 1d. The epoxide 1c (400 mg) in dioxan (10 ml) was heated with 5% $HClO_4$ at 40° for 4 hr. After cooling 5% $NaHCO_3$ aq was added, the product was extracted with ether and worked-up. The crystalline diol (405 mg, 92%) 1d was obtained, m.p. 133–134° (chloroform-hexane). Found: C, 73.55; H, 10.29. Calc. for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27%. MS(*m/e*): 196, 178, 160, 149, 137, 134, 131, 110, 97, 67(base peak); IR($CCl_4$): 3629, 3590 (measured at $10^{-3}$ concentration); $^1H$ NMR: 0.98–2.25mt, 2.47mt (2H), 3.21d(J = 4.40 Hz, 2H); $^{13}C$ NMR: 75.5d, 43.6d, 42.5d, 31.3t, 29.0t, 22.3t.

7,8-*Dihydroxy*-cis,syn,trans-*tricyclo*[7.3.0.$0^{2,6}$]*dodecanes* 2d, 2e. The epoxide 2c (400 mg) was hydrolysed as described for 1d to yield a mixture of 2d and 2e which were separated on a silica gel column (elution with ether).

*Compound* 2d. (170 mg, the lower $R_F$-value), m.p. 125–126°. Found: C, 73.55; H, 10.38. Calc. for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27%. MS(*m/e*): 196, 178, 160, 149, 137, 135, 134, 110, 97(base peak), 67; IR($CCl_4$): 3628, 3592 $cm^{-1}$ (measured at $10^{-3}$ M concentration); $^1H$ NMR: 1.15–2.27mt, 3.22mt; $^{13}C$ NMR: 80.2d, 76.8d, 47.9d, 44.6d, 44.1d, 42.4d, 28.3t, 28.2t, 27.9t, 23.2t.

*Compound* 2e. (230 mg, the higher $R_F$-value): m.p. 122–123°. Found: C, 73.55; H, 10.38. Calc. for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27%; MS(*m/e*): 196, 178, 160, 149, 137, 134, 110, 97(base peak), 67; IR($CCl_4$): 3631 $cm^{-1}$ (measured at $10^{-3}$ M concentration); $^1H$ NMR: 1.22–2.43mt (peaks at 1.61 and 2.18), 3.89mt (2H); $^{13}C$ NMR: 72.2d(2C), 41.7d, 40.2d, 37.5d(2C), 28.3t, 27.0t, 25.7t, 24.5t(2C), 21.9t.

7 - *Hydroxy* - cis,anti,cis - *tricyclo*[7.3.0.$0^{2,6}$]*dodecane* 1e. 1 (400 mg) was hydroborated by the standard procedure[10] to yield the oily product which was separated on a silica gel column (elution with hexane–ether, 1:1). Two compounds were obtained: a hydrocarbon (40 mg, 10%), identical (GC and GC/MS, column *A*, 100°) with 1a; an unseparable mixture of alcohols 1e (350 mg, 79%). Found: C, 79.71; H, 11.25. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%. MS(*m/e*): 180, 179, 178, 162, 133, 121(base peak), 94, 80, 79, 67; IR($CHCl_3$): 3629, 3400, 1095, 1060, 1020 $cm^{-1}$.

cis,anti,cis-*Tricyclo*[7.3.0.$0^{2,6}$]-7-*dodecanone* 1f. 1e (300 mg) was oxidized with pyridinium chlorochromate[11] (600 mg) in $CH_2Cl_2$ (5 ml). After 1 hr stirring ether (20 ml) was added, the soln was filtered through a short silica gel column, solvents were evaporated and the residue was distilled at 170–180°/1.7 kPa to yield 250 mg (84%) of pure ketone 1f. Found: C, 80.93; H, 10.27. Calc. for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. MS(*m/e*): 178, 149, 137(base peak), 110, 95, 81, 79, 67; IR(film): 1710, 1260, 1230, 1165, 1140 $cm^{-1}$; $^1H$ NMR: 1.24–2.09mt, peaks at 1.64 and 2.29 ppm; $^{13}C$ NMR: 214.5s, 50.5d, 46.0d, 42.9t, 40.7d, 40.0d, 32.9t, 31.6t, 30.5t, 25.2t, 22.9t, 22.6t.

cis,anti,cis-(6,8,8-$^2H_3$)*tricyclo*[7.3.0.$0^{2,6}$]-7-*dodecanone* 1h. LiH (20 mg) was dissolved in $D_2O$ (2 ml) and the soln was added to the soln of 1f (150 mg) and decyl trimethylammonium bromide (20 mg) in THF (5 ml). The mixture was stirred at 20° for 32 hr, then dry ice (300 mg) was added and the product was extracted with pentane. After the usual work-up it was obtained 140 mg (92%) of 1h. MS(*m/e*): 181, 140(base peak), 113, 95, 69, 68, 67. The ketone 1h contained 90.2% $d_3$, 7.7% $d_2$ and 2.1% $d_1$ species.

cis,syn,trans-7- *Hydroxytricyclo*[7.3.0.$0^{2,6}$]*dodecanes* 2f, 2g. 2 (500 mg) was hydroborated by the standard procedure[10] to yield 490 mg of a mixture of 2f and 2g. After separation on a silica gel column (elution with hexane-ether, 2:1) it was obtained: 2f (345 mg), m.p. 56–57° (pentane). Found: C, 80.15; 11.09. Calc. for $C_{12}H_{20}O$: C, 79.95; H, 11.18%. MS(*m/e*): 180, 179, 178, 162, 147, 134, 133, 119, 94, 91, 80, 67(base peak); IR($CHCl_3$): 3622, 3450, 1090, 1065, 1040, 1010 $cm^{-1}$.

*Compound* 2g (95 mg): m.p. 36–38°. Found: C, 79.90; H, 11.25. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%. MS(*m/e*): 180, 179, 178, 162(base peak), 147, 136, 134, 133, 119, 97, 94, 91, 80, 67; IR($CHCl_3$): 3630, 3470, 1080, 1030, 1005, 995 $cm^{-1}$.

cis,syn,trans - *Tricyclo*[7.3.0.$0^{2,6}$] - 7 - *dodecanone* 2h. 2f (300 mg) was oxidized as described for 1f to yield 285 mg (96%) of 2h. Found: C, 80.62; H, 10.03. Calc. for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. MS(*m/e*): 178, 160, 149, 137(base peak), 110, 95, 93, 81, 79, 67; IR(film): 1700, 1295, 1230, 1195, 1145 $cm^{-1}$; $^1H$ NMR: 0.83–2.83mt, peaks at 1.63 and 2.54 ppm; $^{13}C$ NMR: 213.4s, 52.5d, 47.7t, 46.0d, 43.5d, 39.9d, 31.4t, 27.8t, 25.3t, 24.7t, 23.5t, 22.9t.

trans,syn,cis - *Tricyclo*[7.3.0.$0^{2,6}$] - 7 - *dodecanone* 2i. 2g (60 mg) was oxidized as described for 1f to yield 50 mg (84%) of 2i. Found: C, 81.11; H, 10.09. Calc. for $C_{12}H_{18}O$: C, 80.85; H,

10.18%. MS(*m/e*): 178, 160, 137, 134, 131, 123, 117, 110, 95(base peak), 81, 79, 67; IR(film): 1712, 1190 $cm^{-1}$.

cis,syn,trans - (6,8,8-$^2H_3$)*Tricyclo*[7.3.0.0$^{2,6}$] - 7 - *dodecanone* 2j. 2h (200 mg) was deuterated as described for 1h to afford 180 mg of 2j which contained 92.8% $d_3$, 5.0% $d_2$ and 2.2% $d_1$ species. MS(*m/e*): 181, 163, 152, 140(base peak), 135, 68, 67.

trans,syn,cis - (6,8,8-$^2H_3$)*Tricyclo*[7.3.0.0$^{2,6}$] - 7 - *dodecanone* 2k. 2i (20 mg) was deuterated as described for 1h to yield 15 mg of 2k which contained 92.5% $d_3$, 4.6% $d_2$ and 2.9% $d_1$ species. MS(*m/e*): 181, 163, 152, 140, 113, 95(base peak).

*Huang-Minlon reduction of* 1f, 2h *and* 2i. 1f (200 mg) was heated with 100% hydrazine hydrate (300 mg) in diethylene glycol (5 ml) at 130° for 4 hr. Then KOH (200 mg) was added and the mixture was heated under argon at 220° for 5 hr. After cooling, water was added and the product was extracted with pentane. The usual work-up afforded 130 mg (71%) of a mixture of 1a (80%) and 1g (20%).

A mixture of 2h and 2i was reduced in a similar manner to yield mainly 2a (90% of the product) together with a small amount of another tricyclododecanes which were different from 1a and 1g.

## REFERENCES


[1]K. Isagawa, K. Tatsumi and Y. Otsuji, *Chem. Letters* 1145 (1976).

[2]K. Isagawa, K. Tatsumi, H. Kosuki and Y. Otsuji, *Ibid.* 1017 (1977).

[3]H. Antropiusová, V. Hanuš and K. Mach, *Transition Met. Chem.* 3, 121 (1978).

[4]H. Antropiusová, K. Mach, V. Hanuš, F. Tureček and P. Sedmera, *React. Kinet. Catal. Lett.*, in press.

[5]G. W. Parshall, *J. Mol. Catalysis* 4, 243 (1978).

[6]S. Dzierzgowski, R. Giezynski, S. Pasynkiewicz and M. Nizynska, *Ibid.* 2, 243 (1977).

[7]S. Landa and J. Vaněk, *Coll. Czech. Chem. Commun.* 35, 3733 (1970).

[8]E. L. Eliel, *Stereochemistry of Carbon Compounds*, p. 290. McGraw-Hill, New York (1962).

[9]H. O. House, *Modern Synthetic Reactions* (Second Edn), p. 19. Benjamin, Menlo Park (1972).

[10]H. C. Brown, *Organic Syntheses Via Boranes*, p. 17. Wiley-Interscience, New York (1975).

[11]E. J. Corey and J. W. Suggs, *Tetrahedron Letters* 2647 (1975).