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Direct Access to Substituted Brendane Derivatives by Palladium-Copper Mediated Cyclisation of *endo*-5-Vinyl-2-norbornene. X-ray Structure of the σ–π Intermediate Palladium Complex. Further Evolution (Baeyer-Villiger Oxidation) to the Quinane System

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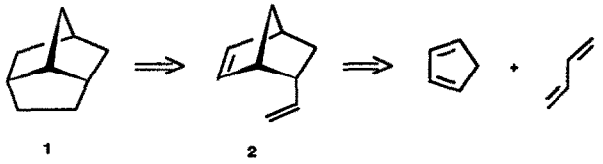
Key Words: non conjugated dienes, nucleophilic addition, intramolecular insertion of double bond into Pd-C bond, reoxidation with molecular oxygen, Oxone.

Abstract: A one-step synthesis of disubstituted brendane derivatives is described starting from (commercially) available vinyl norbornene by the Wacker-type oxidation with $PdCl_2/CuCl_2$ or $PdCl_2/CuCl_n/O_2$ (n=1,2). In addition to the formation of a new carbon-carbon bond two different nucleophilic groups are incorporated with complete chemio-, regio- and high (>90%) stereoselectivity. The NMR and X-Ray structure analysis of a σ-π-palladium-bipyridine complex clearly establishes the stereochemistry of the prerogative intermediate and the position of the coordinated vinyl group in an 'extracyclic' position before the insertion-cyclisation step. This stereochemistry establishes the oxidative cleavage of the cyclised (*cis*-insertion) organopalladium intermediate to proceed with predominant (90%) inversion of configuration. A further ring opening reaction *via* Baeyer-Villiger oxidation has been developed showing the usefullness of the brendane derivatives for an easy access to functionalized quinane system(s) with complete stereocontrol of 5 stereogenic centers.

Introduction. As a part of our studies on the palladium-catalysed oxidative transformation of simple olefins[1] and non conjugated dienes[2] we were intrigued by the possibility of a rapid access to the tricyclic framework brendane 1[3] via cyclisation of suitable non conjugated dienes, such as the Diels-Alder adduct 2 (Scheme 1).[4]



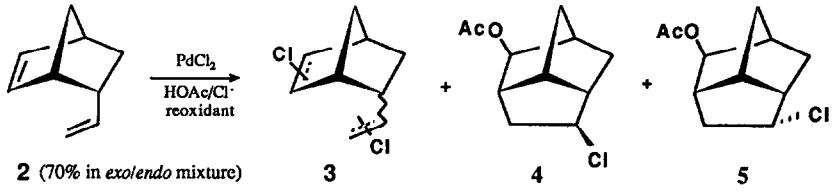
1 2

Scheme 1.

Brendane (tricyclo[4.2.1.$0^{3,7}$]nonane) is a member of the tricyclic C9-family together with brexane,[5] noradamantane[6] or twistbrendane.[7] These structures have been extremely valuable in evaluating mechanistic concepts such as carbene or ionic rearrangements,[8,9] stereochemistry of anionic reactions,[10] mechanistic studies of 1,3 elimination via carbonium ion intermediates or photorearrangement.[11] Furthermore, chemoselective and regiospecific ring opening of these systems should offer an entry into annelated ring systems in the quinane and other annelated series which are members of important natural products.[12] The first brendane derivative has been

observed via homoenolate rearrangement of brexanone under strong basic conditions.[10] In the following time other reactions have been shown to lead to this skeleton notably transposition reactions from brexane[13], twist brendane,[14] noradamantane,[15] spirocyclopropane substituted norbornenes[16] and homocubane.[17] Hydrogenation of deltacyclane and isodeltacyclane[18] are also ways to this systems such as Tl(III) cleavage of the cyclopropane ring in triaxane,[19] intramolecular carbonium ion[20] or carbene[21] addition of 2- or 7-substituted norbornene derivatives, and finally transannular carbene insertion in the bicyclo[4.2.1]nonane system.[22] Most of these routes are cumbersome and lead, in general, to reaction mixtures. More suitable syntheses[23] involve intramolecular addition reactions of *endo* substituted, saturated[24] or unsaturated[25] norbornane compounds. Prior to our preliminary reports[4] that *endo* 5-vinyl-2-norbornene cyclises via Pd(II) oxidation, the brendane skeleton has been obtained (in low yields) with this transition metal under carbonylation conditions[26] or with HCN as a nucleophile.[27] The starting material, 5-vinyl-2-norbornene which is readily available[28] gives a stable σ–π complex[29] but it was not apparent that it would cyclise easily with Pt or Pd catalysis.[30]

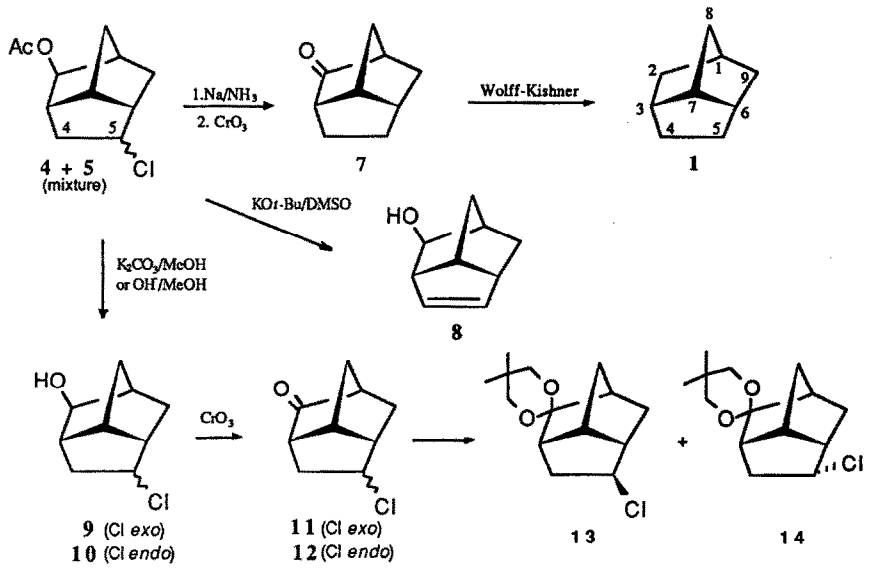
Ring closure to brendane derivatives. Treatment of *endo*-5-vinyl-2-norbornene **2** (isomeric mixture *endo*/*exo*=7/3) with the Wacker-type catalyst system $PdCl_2/CuCl_2$/buffered acetic acid leads, at 80°C after 1 day to a reaction mixture that contains 2 kind of products: first a multitude of unseparable chlorinated, non cyclized compounds of type **3** (40-50%, together with unreacted *endo*-5-vinyl-2-norbornene), which are the result of direct, non Pd-catalysed chlorination[31] of diene **2** (and its *exo* isomer), and second a set of difunctionalized compounds containing two different chloroacetates **4** and **5** (50-60%), which are cyclized, disubstituted brendane derivatives. Chromatographic separation on silica gel (conditions with solvent gradient or Flash-conditions) proved troublesome, since the fractions with the cyclized products tended to be contamined with chlorinated non-brendane compounds. A slightly lower content of chlorinated byproducts is obtained when small amounts of PPh_3 are added. The chlorination of olefins under Wacker type[32] reaction conditions can be reduced by modifying the reoxidation system. For this purpose oxidants like hydrogen peroxide, alkyl hydroperoxides or simply benzoquinone have been introduced as reoxidants.[32,33] For the cyclisation of *endo*-5-vinyl-2-norbornene **2** H_2O_2, benzoquinone or benzoquinone/MnO_2[2c] proved unsatisfactory. A better system was found with the combination of (reduced quantities) $CuCl_2$ and LiCl together with molecular oxygen. The yields of **4**/**5** (isomeric ratio 9:1) could be improved up to 77% and at the same time the presence of chlorinated byproducts was considerably reduced. Under these conditions it is possible, by careful Kugelrohr distillation, to obtain reaction products that are pure enough for microanalysis. Furthermore, the oxygen uptake can be followed, and the optimal ratios of catalyst to copper and lithium chlorides (Pd:Cu:Li=1:15:54) have been determined. Replacement of $CuCl_2$ by CuCl does not alter yields and isomeric ratio of **4** and **5**.



2 (70% in *exo*/*endo* mixture) **3** **4** **5**

Scheme 2.

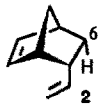
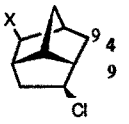
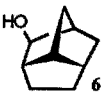
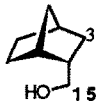
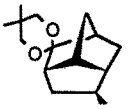
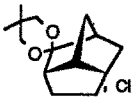
Other metal chlorides (NaCl, KCl, $CaCl_2$) can be used but LiCl gives the best results. The structures of **4** and **5** have been established by NMR analysis and degradation reactions to known brendane derivatives. Reduction with lithium in liquid ammonia and subsequent CrO_3 oxidation according to H. C. Brown[34] yielded brendane-2-one **7**[5,18a,35] via *exo*-2 brendanol **6**.[5,18a,21] The parent hydrocarbon **1**[36] was accessible by Wolff-Kishner[5a,37] reduction. In order to determine the position and the stereochemistry of the chlorine the following transformations have been carried out. This unambiguously permitted to attribute structures **4** for the major and **5** for the minor diastereoisomer, respectively. Base catalysed elimination of HCl from **4** and/or **5** (KO*t*-Bu/DMSO) lead to *exo*-4 brenden-2-ol **8**[38] which contained small amounts of **9** and/or **10**. The difficult but effective elimination of the chlorine is a good indication for its position in the ethano bridge of the new five-membered ring. Only in this part of the brendane structure β-elimination is possible. The rigid and completely eclipsed conformation of substituents at C_4 and C_5 renders HCl elimination effectively unfavourable.



Scheme 3.

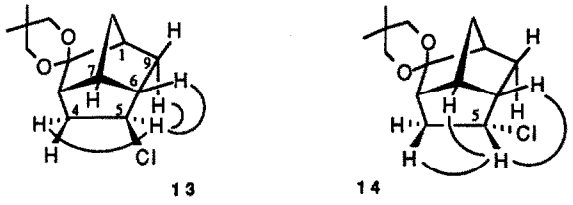
It remained to be shown the exact position and relative configuration of chlorine substituents. The 100 MHz proton spectra of **4** and **5** were only partly exploitable for this purpose. From mechanistic considerations we concluded the C_5 position. Nevertheless, as a simple hint, the typical high field resonance pattern at δ 0.76 ppm indicated a 'normal' $H9_{endo}$ resonance in **4** typical for vicinal, non disturbing CH- or CH_2 groups.[39] Some high field resonances of this type of protons in substituted norbornanes or brendanes can be found in Table 1. Consequently **4** should be the *exo* isomer and **5** its epimer without the characteristic $H9_{endo}$ signal.

Table 1. Chemical shifts of *endo* protons[a] at C_6 in **2**, C_3 in **15**, C_2 in **1** and C_9 in other brendane derivatives

δ (ppm)		δ (ppm)		δ (ppm)
	0.8		X=OAc 0.76 X=OH 0.61	 0.57
	0.6		1.01	 1.7
	0.79b)	13 Cl		14

a) pattern (eg. **6**): part of an AB, d,t J_1 12.7, J_2 2.4Hz, b) ref 22

In order to confirm these structure assignments by complete NMR analyses we decided to introduce a more bulky group which was supposed to split the NMR signals and which, at the same time, should allow easier preparative separation of the two stereoisomers. Hydrolysis (K_2CO_3/MeOH), oxidation[34] and ketalisation with 2,2-dimethyl-1,3-propanediol transformed the reaction mixture **4** and **5** into **13** and **14**, respectively, without affecting the Cl substituent. Effectively these two compounds are easily and quantitatively separated with conventional column chromatography on silicagel. The (400 MHz) spectra of both compounds **13** and **14** showed separated signals for nearly every proton, with the less globular structure **13** being perfectly splitted. The exact attribution of every carbon and and proton as well as complete correlation of all protons could be performed with heteronuclear C-H and H-H COSY experiments. The results have been confirmed by Rotatory-Frame Overhauser Enhancement spectroscopy (ROESY) and NOESY techniques. Selected Nuclear Overhauser Enhancement in **13** and **14** are demonstrated in Figure 1.

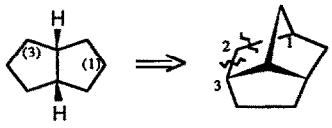


13 **14**

Figure 1. Representation of 5-*exo*- and *endo*-substituted brendanes showing selected NOE interactions of H_5.

Baeyer-Villiger (BV) ring cleavage of brendane derivatives. The cyclisation of *endo*-5-vinyl-2-norbornene **2** leads to brendane compounds that contain two interesting functionalities for further transformations. The incorporation of acetate at C_2 makes **4** and **5** (after transformation to ketones) interesting candidates

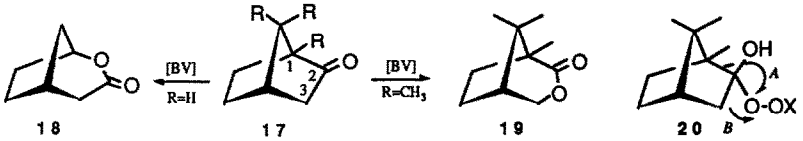
for Baeyer-Villiger[40] transposition reactions. In ketones **11** and **12** (or **7**) cleavage nearby the carbonyl breaks a ring that is different from the one that has been formed with palladium. Annelated (and substituted) bicyclo[3.3.0]octanes become accessible in a simple and straightforward way.



16 **1**

Scheme 4.

BV oxidation is well studied with cyclic and bicyclic ketones, including brendane-5-one.[10,41] In norcamphor **17** (R=H) the C_1-C_2 bond is preferentially cleaved whereas in the more sterically crowded camphor **17** (R=CH_3) the bond breaking takes place at C_2-C_3.[42] The latter result has been explained by *endo* attack of the oxidant at the camphor carbonyl group and the carbon migration according to path *B* via the more favorable chair form transition state contrary to path *A* leading to a boat form transition state (**20**). These arguments have been revised later and the (pure) steric arguments have been complemented by conformational arguments.[40]



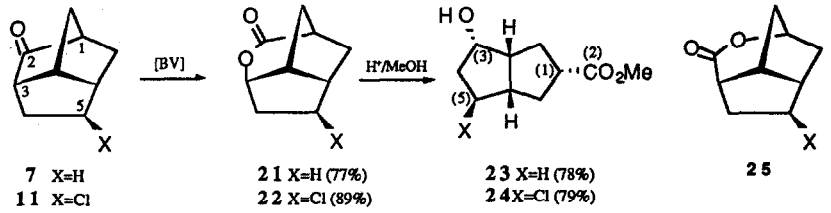
18 **17** **19** **20**

Scheme 5.

In brendane derivatives **7**,**11** or **12** there should be a huge preference for *exo* attack[11a] of the oxidant on the carbonyl group and consequently, bond cleavage was anticipated at C_1-C_2 bond distant to the 'ethano bridge'.

When chloroketone **11** was submitted to Oxone§,[43] oxidation in the presence of wet alumina, a single tricyclic lactone **22** was obtained in 77% yield. Use of *m*-chloroperbenzoic acid in CH_2Cl_2[44] or H_2O_2-CF_3CO_2H[45] led to the same compound with slightly lower yields (60-66%). The new lactone was easily methanolysed (BF_3-OEt_2, methanol) to **24** (numbering in parantheses coresponds to the brendane carbons). Surprisingly, the structure of **22**, which was clearly established from the NMR spectra using 2D correlation experiments showed the chlorine present in the same ring than the (lactone) alcohol group. This means that the norbornane part in the brendane ring had been broken at C_2-C_3 and not at C_1-C_2 (formation of **25**), as anticipated before.

§ Potassium persulfate, $KHSO_5$, when used in the mixture $2KHSO_5$, $KHSO_4$, K_2SO_4. Oxone, a registered trade mark of E. I. du Pont de Nemours and Co. is a versatile although not too common oxidant.



Scheme 6.

The same reaction sequence has been performed with chlorine free brendanone **7** (Scheme 6). The tricyclic lactone **21** has also been obtained from **22** by Bu_3SnH reduction.[46]

Stereoelectronic effects[47] take into account for regioselectivity of the BV oxidation of **7** and **10**. From the possible transition states, conformation **26** represents the least steric hindrance between the leaving group 'OX' and the ethano bridge, as well as (*endo*) OH and H9*endo*.

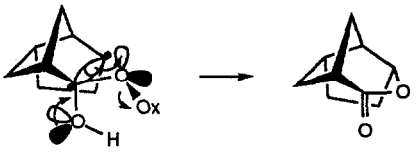
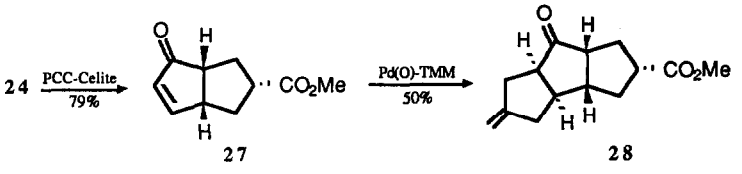


Figure 2. Stereoelectronic effects in the BV cleavage of **7** (and **10**).

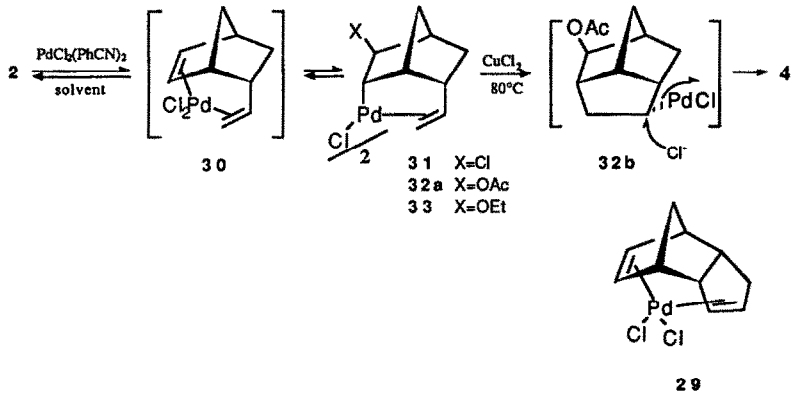
The structure of **24** is interesting for further evolution to the triquinane framework via trimethylenemethane (TMM) methodology.[48] The effective precursor **27** is obtained in good yields directly from **24** with chromium(VI) oxide (PCC, Celite). Consecutive treatment with 1 equivalent of 2-[(trimethylsilyl)methyl]prop-2-en-1-yl acetate in the presence of palladium acetate (0.05 equiv.) and triisopropyl phosphite (0.35 equiv.) leads to the expected *cis:anti:cis* triquinane **28**. This assignment is made from the ^{13}C NMR spectra[49]. The signals of $CHCO_2Me$ (51.0 ppm) and both neighbouring CH_2 groups (32.3 and 35.6) remain nearly unaffected by the new *exo*methylenecyclopentane ring with respect to enone **27** or the more related alcohol **24**.



Scheme 7.

Discussion. The multistep cyclisation of *endo*-5-vinyl-2-norbornene **2** to disubstituted brendanes is an extension of the 1,2-addition of acetate and chloride to simple olefins under Wacker type reaction conditions[32] in

acetic acid.[50,51] Between the initial nucleophilic addition of acetate and palladium, and the oxidative cleavage of a C-Pd σ-bond[52] (with copper chloride) the insertion of a second double bond takes place in **2**. This type of *cis*-insertion of a unsaturated ligand is the C-C bond forming step in many palladium-catalysed cyclisation reactions.[53] Such (stoichiometric) reactions with norbornane- and nortricyclyl-palladium complexes have been described by Vedejs[54] and Larock.[55] Variants of this cyclisation with catalytic amounts of Pd(II) have been studied by others[56,57] and us[2b-e,4] on 1,5-dienes involving mono-, di- and trisubstituted dienes. Trost reported on an example with 1,6-dienes.[58] The mechanism of brendane formation is outlined in Scheme 8.

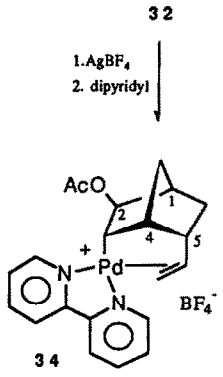


Scheme 8.

The first step is the coordination of palladium chloride to the diene. This is well known with 1,5-dienes and such stable and isolable Pd complexes, eg. the structurally related dicyclopentadiene complex **29**[59] have been extensively studied.[60] *endo*-5-Vinyl-2-norbornene is one of the rare 1,5-dienes where the di π-Pd olefin complex cannot be isolated despite the possible chelation to a reactive norbornene and vinylic double bond. No coordination from the *exo* side to the norbornene structure takes place since no products from such reactivity[50,55,61] are found. Nucleophilic addition[62,63] of OAc^- (*exo*) to *endo*-coordinated **2** gives **32a**. The stereochemistry[60] usually observed is *trans* though with norbornene *cis* addition has been described.[1c,50] When 5-vinyl-2-norbornene is treated with $PdCl_2$ at room temperature nucleophilic addition of Cl, OAc or OR takes place and the stable σ–π complexes **31-33** are isolated in high yields.[29] The incorporated anion depends on the solvent used; interestingly the interchange between these three nucleophiles is easy and reversible. **32a** is effectively an intermediate in the catalytic formation of brendane derivatives, most probably in equilibrium with **31** since both the chloride and acetate chloro complexes are easily transformed to **4** and **5** (ratio 7:3) with $CuCl_2$ in acetic acid (3h, 80°, yields 50-60%). In case of **31** also small amounts of the chlorides **3** are detected in GC. The exact geometry of the vinylic double bond is of interest for the steric proceeding of the cyclisation step, but also for mechanistic implications of the last, oxidative cleavage[52] in the cyclised product. Wipke and Goeke[29] dicussed this problem but the low field NMR spectra did not give clear answers to the problem. We succeeded in isolating suitable crystals (acetonitrile) of the cationic palladium complex **34** readily obtained from **31** with $AgBF_4$ and

2,2'-bipyridine. The results of the X-ray diffraction study are summarised in Tables 2,3 and 4 and illustrated in Fig. 3.

The structural features of **34** are as expected. It turns out that the vinyl group is coordinated to the palladium with a value close to carbon-palladium σ-bond. Norbornane C-Pd distances range between 2.024 (C_3) (Pd σ-bond), 2.202 (C_8) and 2.139 Å (C_9) (Pd π-bond).



Scheme 9.

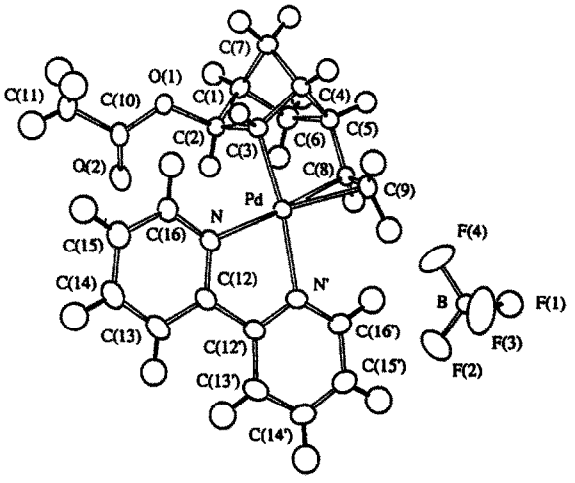


Figure 3. Perspective view of **34**

The C-C bond lengths in the norbornane ring average 1.537 Å, a value few different to the ideal tetrahedral value. As a consequence of the coordination the bicyclic system is slightly distorted since all carbon-carbon distances are different, the shortest C-C bond being C_4-C_7 with 1.508 Å. At this side of the molecule the *endo* vinyl-norbornane bond, C_5-C_8 (1.488 Å) is even smaller. A similar distortion effect is visible in the dipyridine ligand. The bond distances vary 0.046 Å (C-N) and 0.03 Å in the aromatic C-C bonds.

The central Pd atom is mainly in a square-planar environnment, defined by the 2 nitrogen atoms of dipy (N,N'), C_3 (norbornane) and the (roughly) perpendicular C-C double bond (C_8=C_9). The coordination to the vinyl group, which deviates from the perpendicular plane to about 30°, is not symmetric, the Pd is much closer to C_9 (2.139 Å) than to C_8 (2.202 Å).

The internal angles of the norbornyl substituent deserve no special mention, the C-C bond angles range from 95.6° (C_1-C_7-C_4) to 105.09° (C_6-C_1-C_2) with a mean value of 102.4. The C-C-C_{vinyl} angles are slightly enlarged from 110.4° (C_4-C_5-C_8) to 115.5° (C_6-C_5-C_8).

The X-ray structure (Fig. 3) clearly shows the predicted (NMR, mechanism) configuration of the acetate (*exo*), the carbon-palladium σ-bond (*endo*), and, most important, the geometry of the vinyl group in this complex. With dihedral angles of -154° (C_6-C_5-C_8-C_9) and 81° (H_5-C_5-C_8-C_9) the vinyl double bond is pointing out of the bicyclic ring system. In solution this form might be in equilibrium with the more strained 'inside' configuration. These type of equilibria of coordinated double bonds in σ–π complexes has been shown in other dienes e.g *cis* 1,2-divinyl cyclohexane.[64] On the other side interpretation of the high field NMR spectra of **34** confirms the crystal structure. The bridgehead proton H_5 (2.68 ppm) shows couplings with H_3,H_4 and

H6*endo/exo*, but not with H8 which indicates a dihedral angle H5/H8 of about 90°. Spatial neighbourhood between H4 (3.07 ppm) and the vinylic H9 (5.22ppm) is indicated by a NOE effect (6.51%) in the NOE difference spectrum. This excludes the conformation (90°) with the double bond inside the norbornane ring. It also explaines the instability of the di π-palladium complex requiring the 'inside', for the complex formation favourable, diene conformation.

The insertion of the double bond into the Pd-C bond (cyclisation) is the slow, rate determining step and requires heat (80°C). This energy demand is not surprising when taking into account the X-ray data which indicated that C9 is closer to the palladium than C8, but the new carbon-palladium bond is formed with C8. Additionally, the four-membered transition state of the insertion requires *cis* stereochemistry,[65] and in the resulting palladium σ- complex the palladium points under the norbornane ring. The final reaction step is the cleavage of the C-Pd bond in the cyclised complex **32b**. Formally this can proceed *via* reductive elimination. However, in the presence of oxidants such as Cu(II) chloride it has been shown to proceed with inversion of configuration.[66,67] The S_N2 type cleavage is nicely demonstrated by the (predominant) exo stereochemistry of the Cl substitutent in the brendane. High chloride concentration is known to increase the S_N2 character of the oxidative cleavage of C-Pd σ-bonds.[67] The formation of higher amounts of the *exo* isomer **4** when the stoichiometric $CuCl_2$ conditions are switched to catalytic $CuCl_2/LiCl/O_2$ is another example for the important role of the reoxidation system for selectivity control. A concurrent, sometimes exclusive mode of cleavage involves the formation of carbonium ions,[68] which may rearrange,[1c,50] or simply render the transformation less selective[69] by randomisation of the secondary carbon atom. Despite numerous reactions with various chloride concentrations conditions for complete exclusion of the ionic mechanism could not be found.

The organopalladation-olefin insertion of *endo*-5-vinylnorbornene-2 is a unique Pd catalysed reaction sequence. It is completely regio- and chemoselective, but also highly stereoselective. β-Elimination is avoided by stereochemical reasons but also rearrangements are not encountered. The two nucleophilic groups are introduced in strategical useful positions which allows the formal dimerisation (quinane) or trimerisation (triquinane) of cyclopentadiene. It may open new applications of vinyl norbornenes offering interesting complements to the usually observed Cope rearrangements with these systems.[70]

Experimental Section

IR spectra were recorded on a Perkin Elmer 257 spectrometer with the absorption maxima in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 100, 200 and 400MHz FT spectrometers (^{13}C at 25.1, 50.3 and 100.6MHz). All spectra were taken in $CDCl_3$ or CD_3COCD_3 using the residual solvent peak as internal reference. Chemical shifts are given in ppm relative to Me_4Si. DEPT spectra were determined to assign carbon multiplicities (C, CH, CH_2, CH_3), 2D carbon-proton and proton-proton COSY, as well as NOE difference and ROESY experiments were used for determination of the structural relationships of compounds **9**, **11**, **13**, **14**, **22**, **23**, **24**, **28** and **34**. Flash chromatography was performed according to Still[71] on silica gel 60 (230-400 mesh, Merck). If not other specified the following 'simple' chromatography was done for 1-2mmol

reactions: silicagel 60 (10-250 mesh, 4 g), 20 mL fractions with the following gradient 0, 1, 2, 5, 10, 20 and 50% ether/hexane. Thin layer chromatography was performed on aluminium sheets pre-coated with Merck DC-Alufolien 60 F_{254} plates. The plates have been visualized with UV light or developed with 5% phosphor ammonium molybdate in absolute ethanol and heat. Microanalyses were performed by the 'Service de Microanalyse de la Faculté de St.-Jérôme' in Marseilles, France. *endo*-5-Vinyl-2-norbornene **2** was purchased from from Aldrich as an *exo/endo* mixture (3:7). For the oxidation of secondary alcohols a chromic acid solution was prepared according to H.C. Brown[34] with sodium dichromate dihydrate (100 g, 330 mmol), concentrated sulfuric acid (136 g, 1.34 mol), and dilution with water to a total volume of 500 mL.

Cyclisation of *endo*-5-vinyl-2-norbornene (2).

Stoichiometric $CuCl_2$. $PdCl_2$ (250 mg, 1.4 mmol), $CuCl_2$ (12.5 g, 92.5 mmol), PPh_3 (1.5 g, 5.7 mmol) and NaOAc (4.1 g, 50 mmol) were suspended in glacial acetic acid (75 mL). 5-vinyl-2-norbornene (6 g, 50 mmol, 35 mmol *endo* isomer) was added and the mixture heated to 80°C during 24 hours with efficient stirring. After cooling the reaction mixture was filtered from CuCl, poured into 100 mL water and extracted with hexane (3-4 x 75-100 mL). The combined hexane phases were washed to neutrality with saturated bicarbonate and brine and dried over $MgSO_4$. After evaporation of the solvent 7.75 g of a sligtly yellow liquid was recovered. Glc analysis (carbowax type filled columns) showed the presence of a multitude of (unseparable) chlorinated compounds (40-50%) together with *exo*-2-acetoxy-*exo*-5-chlorobrendane **4** and *exo*-2-acetoxy-*endo*-5-chlorobrendane **5** (50-60%). By careful distillation a part of the impurities can be removed b.p. 75-80° C, 0.1-0.3 mm Hg. Total yield of **4** and **5** (ratio 7:3) 4.65 g (62% with respect to *endo* 5-vinyl-2-norbornene).

Catalytic $CuCl_2/LiCl/O_2$ (or $CuCl/LiCl/O_2$). A mixture of $PdCl_2$ (1 g, 5.65 mmol), $CuCl_2$ (11.4 g, 85 mmol), LiCl (16.95 g, 400 mmol), NaOAc (16 g, 200 mmol) and glacial acetic acid (400 mL) were placed in a 1 L one necked flask equipped with an oval magnetic stirring bar. The initially yellow slurry was stirred rapidly for several minutes at r.t. and 5-vinyl-2-norbornene (24 g, 200 mmol, 140 mmol *endo* isomer) was added in one portion. The flask was branched to a reflux condenser equipped with a three way stopcock at its upper end. The stopcock was branched to a graduated 2L vessel filled with pure oxygen. The reaction flask was evaporated (very shortly) and filled with oxygen. The mixture was stirred vigorously (stirring rate higher than 700 r.p.m.) and heated to 80°C until 3.5-3.7 L of O_2 has been consumed (24-32 hours). After addition of water (600 mL) the reaction mixture was extracted with pentane or hexane (1 x 400 mL and 3 x 200 mL). The combined hydrocarbon layers were washed with saturated aqueous solutions of $NaHCO_3$ (2 x 100 mL) and NaCl, dried over $MgSO_4$, filtered and the solvent evaporated. The crude reaction product (36 g) was distilled through a short Vigreux column or by means of an Aldrich Kugelrohr apparatus (80-100° C, 0.3 mmHg). Yield of **4** and **5** (colourless liquid, ratio 9:1) 22.5-25 g (69-77% with respect to *endo* 5-vinyl-2-norbornene), b.p. 92-95° C, 0.3 mmHg. Anal. Calcd. for $C_{11}H_{15}ClO_2$: (mixture of **4** and **5**) C, 61.53; H, 7.04; Cl,16.51. Found: C, 61.48; H, 7.48; Cl, 16.40. **4** and **5** have been separated by preparative GC (carbowax 4000, 160° C).

***exo*-2-Acetoxy-*exo*-5-chlorobrendane (4).**

IR (neat) 2900, 1740, 1250, 1030 cm^{-1}. ^1H NMR (200 MHz) δ 4.24 (dd, J_1 7, J_2 2 Hz, 1H, H_5), 4.15 (br s, 1H, H_2), 2.80 - 2.88 (m, 1H), 2.51 (dd, part of an AB, J_1 15.4, J_2 7 Hz, 1H, H_4), 2.12 - 2.45 (m, 3H),

2.02 (s, 3H, CH_3), 1.75 - 1.95 (m, 3H), 1.52 (dd, $J_1$10.6, J_2 1Hz, 1H), 0.76ppm (dt, J_1 13.6, J_2 2.6 Hz, 1H, H9*endo*); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 170.4 (CO), 85.9 (C_2), 65.8 (C_5), 49.8 (C_3), 47.9 (C_6 and C_7), 44.5 and 42.5 (C_4), 40.9 (C_1), 35.4 (C_9), 32.0 (C_8), 21.3 (CH_3). Anal. Calcd. for $C_{11}H_{15}ClO_2$: C, 61.53; H, 7.04; Cl,16.51. Found: C, 61.55; H, 6.99; Cl, 16.77.

exo-2-Acetoxy-_endo_-5-chlorobrendane (5).

IR ($CHCl_3$) 2960, 2880, 1750, 1250, 1030 cm^{-1}. ^1H NMR (100 MHz) δ 4.37 (m and br s superimposed, 2H, H_2 and H_5); 2.2 - 2.75 (m, 4H, H_1,H_3,H_7,H_8); 2.04 (s, 3H, CH_3); 1.7 - 2.05 (m, 2H); 1.4 - 1.7 (m, 4H). ^{13}C NMR (25.1MHz) some values from the mixture **4/5** δ 85.6 (C_2), 61.5 (C_5). Anal. Calcd. for $C_{11}H_{15}ClO_2$: C, 61.53; H, 7.04; Cl,16.51. Found: C, 61.14; H, 7.27; Cl, 16.54.

exo-Brendane-2-ol (6).[18a,21]

In a 250 mL flask equipped with a low temperature cooler liquid ammonia (70 mL) was condensed at -40° C. Na (3 g, 87 mmol) was added in small portions followed by *exo*-2-acetoxy-*exo*/*endo*-5-chlorobrendane (**4/5**) (3.27 g, 15.2 mmol) dissolved in dry ether (7 mL). The mixture was stirred and (slowly) allowed to warm up to room temperature in a way that ammonia was evaporating. Ether (100 mL) was added and unreacted Na was neutralized with ethyl acetate (50 mL). Water was added and the product extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated. The saturated alcohol **6** was purified by flash chromatography, yield 1.1 g (65%), m.p. 133-135° C (lit.[18a] 133.5-134.5). ^1H NMR (400 MHz) δ 3.27 (s, 1H, H2*endo*); 2.22 (m, W/2=10 Hz, 1H); 2.03 (m, W/2=22 Hz, 1H); 1.97 (m, W/2=9 Hz, 1H); 1.58 - 1.9 (m, 9H); 0.57 ppm (d,t, δ=12.7 and 2.4 Hz, 1H, H9*endo*); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 84.4 (C_2), 51.2 (C_3), 46.3 (C_7), 42.9 (C_1), 37.9 (C_6), 35.5 (C_8), 34.6 (C_9), 32.1 (C_5), 29.0 (C_4).

Brendane-2-one (7).[18a]

exo-Brendane-2-ol (**6**) (402 mg, 2.9 mmol) was dissolved in ether (10 mL) and the chromic acid solution[34] (3 mL) was added slowly at 0° C. Stirring was continued for 1 hour at room temperature and and a small quantity of isopropanol was added in order to destroy excess Cr(VI). The phases were separated und the aqueous layer was extracted 3 times with ether. The combined organic phases were washed with bicarbonate solution and brine. After drying over $MgSO_4$, filtration, evaporation of the solvent the residue was purified by chromatography. Yield 298 mg (75%), m.p. 117-118° C (lit.[18a] 118.5-119.5). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 221.8 (CO), 52.4 (C_3), 48.2 (C_7), 46.1 (C_1), 37.5 (C_6), 35.0 (C_8), 33.4 (C_9), 32.2 (C_5), 27.6 (C_4).

exo-2-Hydroxy-brend-4-ene (8).[11b]

The mixture **4/5** (370 mg, 1.72 mmol) was dissolved in dry dimethyl sulfoxide (1.5 mL) and added to a solution of potassium *tert*-butoxide (1g,) in DMSO (5 mL). The dark solution was stirred during 1 day. Water (5 - 10 mL) was added and the product extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated. The unsaturated alcohol **8** was purified by flash chromatography, yield 100 mg (43%). IR ($CHCl_3$) 3610, 3450 (br), 3060, 3000, 2950, 2880, 1040, 1015, 910 cm^{-1}. ^1H NMR (200 MHz) δ 5.95 (m, 5 lines, W/2 5.3 Hz, 2H, H_4 and H_5), 3.46 (s, 1H, H2*endo*); 2.92 (m,

W/2 6 Hz, 1H), 2.2 - 2.42 (m, 3H), 2.40 (s, 1H, OH), 2.0 (d, J= 10.5 Hz, 1H), 1.44 - 1.58 (m, 2 superimposed AB patterns, 2H), 1.08 ppm (dt, 1H, $J_1$12.2 J_2 2-3 Hz, 1H, H9*endo*); ^{13}C NMR (50,3 MHz) δ 140.2 (C=C), 135.0 (C=C), 76.8 (C_2), 55.0 (CH), 52.5 (CH), 49.6 (CH), 41.2 (CH), 35.1 (CH_2), 35.0 ppm (CH_2).

***exo*-2-Hydroxy-*exo*-5-chlorobrendane (9).**

exo-2-Acetoxy-*exo*-5-chlorobrendane (**4**) (containing 5-10% of **5**) (4.72 g, 22 mmol) was stirred with K_2CO_3 (3.1 g 22 mmol) in methanol (100 mL) during 2 hours at room temperature. Methanol was evaporated and ether (20mL) was added. The solution was washed with brine, dried over $MgSO_4$, filtered and evaporated. The product was purified by flash chromatography. Small amounts of the 5-*endo* isomer **10** can be removed by Kugelrohr distillation (80-90° C, 5mm Hg), yield 3.8 g (93%), m.p. 60-61° C. IR (neat) 3610, 2970, 2880, 1450, 1310, 1150, 1070, 1020, 955, 910 cm^{-1}. ^{1}H NMR (400 MHz) δ 4.17 (dd, J_1 7 J_2 2.5 Hz,1H, H_5); 3.28 (s, 1H, H2*endo*); 2.8 (m, W/2 9 Hz, 1H), 2.35 (ddd, J_1 16 J_2 7 J_3 1.5 Hz,1H, H_4), 2.31 (m, W/2 10 Hz, 1H), 2.25 (ddd, J_1 16 J_2 8.5 J_3 1.2 Hz,1H, H_4), 2.08 (m, W/2= 9 Hz,1H), 2.02 (m, W/2 15 Hz, 1H), 1.94 (ddd, J_1 10.6 J_2 3.5 J_3 2 Hz,1H, H_8), 1.76 (ddd, J_1 13.5 J_2.5 J_3 4.8 Hz,1H, H9*exo*), 1.6 (m, W/2 15 Hz, 1H), 1.46 (dd, J_1 10.6 J_2 1.2 Hz, and other small couplings, 1H, H_8), 0.61 ppm (dt, J_1 13.5 J_2 2.5 Hz,1H, H9*endo*); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 83.8 (C_2), 66.0 (C_5), 49.6 and 49.4 (C_3 and C_6), 44.3 and 43.3 (C_1 and C_7), 42.6 (C_4), 34.8 (C_8), 31.9 (C_9). Anal. Calcd. for $C_9H_{13}ClO$: C, 62.61; H, 7.59; Cl,20.53. Found: C, 62.58; H, 7.53; Cl, 20.36.

***exo*-5-Chlorobrendane-2-one (11).**

exo-2-Hydroxy-*exo*-5-chlorobrendane (**9**) (3.59 g, 20.7 mmol) in ether (70 mL) was oxidized with the chromic acid solution[34] (22 mL) as described for the preparation of **7**. Yield of **11** 3.4 g (94 %) (containing sometimes small amounts of the 5-*endo* isomer **12**). IR ($CHCl_3$) 2960, 2880, 1745, 1050 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (d, J 7.2 Hz, 1H, H5*endo*), 3.11 (m, W/2 11 Hz, 1H, H_7), 2.63 (d, J 11,3 Hz 1H, H_6), 2.43 (m, W/2 6 Hz, 1H, H_1), 2.3 - 2.4 (m, 2H, H_4 and H_3), 2.17 - 2.26 (m, 1H, H_4), 1.88 - 1.97 (d, 1H, H9*exo*), 1.82 (d, part of an AB, J_1 11 Hz, 1H, H8*syn*), 1.66 (dd, part of an AB, J_1 11.0, J_2 = *1* Hz, 1H, H8*anti*), 0.95 (d, part of an AB, J 13.7 Hz, 1H, H9*endo*). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 218.7 (CO), 64.9 (C_5), 50.3 (C_3), 49.0, 48.1 (C_6 and C_7), 44.1 (C_1), 40.7 (C_4), 33.6 (C_8), 31.0 (C_9). Anal. Calcd. for $C_9H_{11}ClO$: C, 63.35; H, 6.50; Cl, 20.53. Found: C, 63.13; H, 6.54; Cl, not performed.

***endo*-5-Chlorobrendane-2-one (12).**

The *endo* isomer **12** has been obtained by flash chromatography of a mixture of *exo*- and *endo*-5-Chlorobrendane-2-one (**11/12**). ^{1}H NMR (400 MHz) δ 4.41 (ddd, J_1 10 J_2 6.4 J_3 5.8 Hz,1H, H5*exo*), 2.62 - 2.73 (m, 2H, H_6 and H_7), 2.54 (dt, J_1 14.9 J_2 9.9 Hz,1H, H4*endo*), 2.45 (m, W/2 9 Hz, 1H, H_1), 2.11 - 2/17 (m, 1H, H_3), 1.69 - 1.81 (m, 4H), 1.64 ppm (dt, J_1 13.8 J_2 2.0 Hz and other small couplings,1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 218.7 (CO), 60.7 (C_5), 49.4 (C_3), 46.9, 45.0 (CH_6 and CH_7), 44.9 (CH_1), 38.0 (C_4), 35.0 (C_8), 25.0 ppm (C_9).

Spiro-2-dioxolane-*exo*-5-chlorobrendane (13) and spiro-2-dioxolane-*endo*-5-chlorobrendane (14).

A mixture of *exo*- and *endo*-5-chlorobrendane-2-one (**11** and **12**) (4 g, 23 mmol, ratio 7:3, from the stoichiometric $CuCl_2$ reaction) was treated with 2,2-dimethyl-1,3-propanediol (2.4 g, 23 mmol) and *p*-toluenesulfonic acid (35-50 mg) in benzene (60 mL). Water was trapped by means of a Dean-Stark apparatus. The solution was washed with some mL of aqueous $NaHCO_3$ and brine. The solution was dried ($MgSO_4$) and the solid residue (5.5 g) transferred to a silicagel column. Elution with ether/hexane(gradient) yielded pure **13** (1 g), a mixture of **13/14** (1 g) and pure **14** (80 mg).

Spiro-2-dioxolane-*exo*-5-chlorobrendane (13).

^1H NMR (400 MHz) δ 4.19 (dd, J_1 7.5, J_2 2.5 Hz, 1H, H5*endo*), 3.53 (d, part of AB, J 11.3 Hz, 1H of CH_2 in dioxolane), 3.37 (d, part of AB, J 11.0, 1H of CH_2 in dioxolane), 3.35 (d, part of AB, J 11.4, 1H of CH_2 in dioxolane), 3.30 (d, part of AB, J 11 Hz, 1H of CH_2 in dioxolane), 2.8 (m, W/2 12 Hz, 1H, H7), 2.67 (dd, part of AB, J 15.4 and 7.3 Hz, 1H, H4*endo*), 2.61 (m, W/2 8.6 Hz, 1H, H_1), 2.34 (d, J= 11 Hz, 1H, H6); 2.16 (m, W/2 16 Hz, 1H, H3), 1.95 (dd, part of AB, J_1 15.5 J_2 8.5 Hz, and several small couplings, 1H, H5*exo*), 1.78 (d, part of AB, J 10.3 Hz, and small couplings, 1H, H8*anti*), 1.59 (ddd, part of AB J_1 13.5, J_2 11.5 J_3 4 Hz, 1H, H9*exo*), 1.31 (dt, part of AB, J_1 10.4 J_2 1.8 - 2 Hz, 1H, H8*syn*), 1.01 (dt, part of AB, J_1 13.3 J_2 2.5 Hz, 1H, H9*endo*), 0.99 (s, 3H, CH_3) and 0.83 ppm (s, 3H, CH_3); ^{13}C NMR (100,52 MHz) δ 106.3 (C_2), 72.7 (CH_2-O), 71.1 (CH_2-O), 66.5 (C_5), 50.8 (C_7), 48.6 (C_6), 45.6 (C_3), 39.5 (C_1), 37.8 (C_8), 33.4 (C_9), 30.1(C_4), 29.9 (C_{quart}-dioxolane), 22.8 (CH_3), 22.2 ppm (CH_3). Anal. Calcd. for $C_{11}H_{21}ClO_2$: C, 65.49; H, 8.24; Cl,13.81. Found: C, 65.24; H, 8.10; Cl, 13.8.

Spiro-2-dioxolane-*endo*-5-chlorobrendane (14).

^1H NMR (400 MHz) δ 4.35 (ddd, J_1 10 J_2 6.7 J_3 5.3 Hz, 1H, H5*exo*), 3.3 - 3.52 (m, 2 AB spectra, 4H, CH_2dixolane), 2.56 (m, W/2 8 Hz, 1H, H_1), 2.35 (m, W/2 10 Hz, 1H, H7), 2.34 - 2.42 (m, 1H, H6), 2.29 (ddd, J_1 14.6 J_2 10.1 J_3 8.5 Hz, 1H, H4*exo*), 2.09 (ddd, J_1 14.6 J_2 6.8 J_3 1.6 Hz, 1H, H5*endo*), 1.97 - 2.02 (m, 1H, H3), 1.8 (d, J 10.4 Hz, and small couplings, H8), 1.7 (dt, J_1 13.5 J_2 2.5 Hz, 1H, H9*endo*), 1.43 (ddd, J_1 13.8 J_2 11.1 J_3 4.4 Hz, 1H, H9*exo*), 1.39 (d, J 10.3 Hz, and small couplings, H8), 0.95 and 0.91 ppm (2s, 6H, 2 CH_3dioxolane); ^{13}C NMR (100.52 MHz) δ 106.8 (C_2); 72.8 (CH_2-O); 71.0 (CH_2-O); 62.3 (C_5); 46.9 and 46.5 (C_6 and C_7); 46.5 (C_3); 39.9 (C_1); 35.0 (C_4); 34.2 (C_8); 29.9 (C_{quart}-dioxolane); 24.4(C_9); 22.7 (CH_3); 22.3 ppm (CH_3). Anal. Calcd. for $C_{14}H_{21}ClO_2$: C, 65.49; H, 8.24; Cl, 13.81. Found: C, 65.41; H, 8.28; Cl, 13.3.

Baeyer-Villiger (BV) reaction with oxone and humid alumina[43]

General procedure The humide alumina was prepared by shaking vigorously alumina A (type I, 10 g) with water (2 g) obtaining a finely powdered reagent. A slurry of humide alumina, ketone, and oxone in CH_2Cl_2 was stirred under reflux during 3 and a half days under an atmosphere of argon. 3 New portions of oxone were added every 20 hours. The mixture was filtered, the residue washed with CH_2Cl_2 and the filtrate evaporated. Purification by flash chromatography yielded pure lactones.

3-Oxatricyclo[5.2.1.$0^{4,8}$]decan-2-one (21).

The BV reaction on brendane-2-one (7) (500 mg, 3.67 mmol) with humide Al_2O_3 (3.7 g), oxone (3.8 g and 3 x 1.9 g, total 15 mmol) in CH_2Cl_2 (20 mL) afforded 497 mg (89%) of **21**, m.p. 104-108° C. IR (neat) 2960, 2880, 1750, 1550, 1370, 1180, 1050cm^{-1}.^{1}H NMR (400 MHz) δ 4.69 (t, *J* 3.5 Hz, 1H, H_4), 2.8 (t, *J* 4.5 Hz, 1H, H_1), 2.57 (m, W/2 10 Hz, 2H), 1.96 - 2.27 (m, 4H), 1.65 - 1.76 (m, 2H), 1.56 (d, *J* 13.7 Hz, 1H), 1.42 - 1.52 ppm (m, 1H); ^{13}C NMR. (100.6 MHz, $CDCl_3$) δ 175.7 (CO), 86.0 (C_4), 45.2 (CH), 42.0 (CH), 40.6 (CH_2), 38.2 (CH), 34.6 (CH_2), 32.2 (CH_2), 29.9 (CH_2). Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.99; H, 7.98.

***exo*-6-Chloro-3-oxatricyclo[5.2.1.$0^{4,8}$]decan-2-one (22).**

The BV reaction on *exo*-5-chlorobrendane-2-one (**11**) (511 mg, 3 mmol) with humide Al_2O_3 (3.7 g), oxone (3.8 g and 3 x 1.9 g, total 15 mmol) in CH_2Cl_2 (20 mL) afforded 432.7 mg (77%) of **22**, m.p. 134-135° C. IR (neat) 2980, 1760, 1550 cm^{-1}. ^{1}H NMR (400 MHz) (1D COSY experiments) δ 4.80 (tt, J_1 5, J_2 1.2 Hz, 1H, H_4), 4.17 (dt, J_1 2.1, J_2 = 6.8 Hz, 1H, H_{6endo}), 3.01 (q, *J* 5.5 Hz, 1H, H_8), 2.87 (dd, J_1 7, J_2 4 Hz,1H, H_1), 2.82 (m, W/2 15 Hz, 1H, H_7), 2.65 (dd, part of an AB, J_1 15.6, J_2 7.2 Hz, 1H, H_{5endo}), 2.27 (ddd, J_1 14.4,J_2 11.3, J_3 6.7 Hz, 1H, H_{10exo} and ddd J_1 15.5, J_2 6.5, J_3 5 Hz, 1H, H_{5exo}), 2.06 (d, part of an AB, *J* 12.7 Hz, 1H, H_{9syn}), 1.78 (dt, part of an AB, J_1 12.4, J_2 4.4 Hz, 1H, H_{9anti}), 1.64 (dt, part of an AB, J_1 14.6, J_2 2.3 Hz, 1H, H_{10endo}). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.1 (CO), 84.0 (C_4), 63.7 C_6), 51.3 (C_7), 46.7 (C_5), 44.0 (C_8), 41.8 (C_1), 36.4 (C_{10}), 29.8 (C_9). Anal. Calcd. for $C_9H_{11}ClO_2$: C, 57.92; H, 5.94; Cl,19.00. Found: C, 57.93; H, 5.91; Cl, 19.10.

2-*endo*-Hydroxy-7-*endo* carbomethoxy*cis*-bicyclo[3.3.0]octane (23).

3-oxatricyclo[5.2.1.$0^{4,8}$]decan-2-one (**21**) (500 mg, 3.67 mmol) in methanol (20 mL) was treated with boron trifluoride etherate (0.55 mL, 4.05 mmol) at room temperature. After 50 min methanol was evaporated. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with brine (2x), dried over magnesium sulfate, filtered and evaporated. After flash chromatography pure **21** was obtained (containing 5-10% of a second product). Yield 497 mg (89%). ^{1}H NMR (200 MHz) δ 4.13 (q, *J* 6.3 Hz, 1H, H_2), 3.64 (s, 3H, CH_3), 2.35 - 2.75 (m, 3H), 2.1 - 2.27 (m, 1H), 1.3 - 1.92 ppm (m, 8H); ^{13}C NMR (25.3 MHz, $CDCl_3$) δ 175.7 (CO-ester), 73.8 (C_2), 51.1 (CH_3), 48.4, (CH), 45.5, (CH), 41.3, (CH), 38.2 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 27.8 (CH_2).

2-*endo*-Hydroxy-4-*exo* chloro-7-*endo* carbomethoxy*cis*-bicyclo[3.3.0]octane (24).

exo-6-Chloro-3-oxatricyclo[5.2.1.$0^{4,8}$]decan-2-one (**22**) (687 mg, 3.68 mmol) was treated with BF_3xEt_2O as described for **21**. This procedure yielded 625 mg (78%) of **24**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (dt, J_1 5.9J_2 7.6 Hz, 1H, H_2), 4.06 (m, W/2.*12.4* Hz, 1H, H_4), 3.64 (s, 3H, CH_3), 2.63-2.84 (m, 3H, left part H_1, middle part H_7, right part H_5), 2.22-2.31 (m, 1H, H_6), 2.12-2.22 (m, 2H, 2 x H_3), 1.87-1.92 (m, 2H, 2 x H_8), 1.45 (ddd, 1H, J_1 9, J_2 11, J_3 12.9 Hz, H_6). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 175.7 (CO), 72.0 (C_2), 63.2 (C_4), 54.0 (C_7), 51.9 (CH_3), 45.9 (C_1), 45.6 (C_5), 43.1 (C_3), 36.4 (C_6), 29.7 (C_8). Anal. Calcd. for $C_{10}H_{15}ClO_3$: C, 54.93; H, 6.91; Cl,16.21. Found: C, 54.82; H, 6.89; Cl, 16.3.

7-*endo*-Carbomethoxy-*cis*-bicyclo[3.3.0]oct-3-en-2-one (27).

Celite (1.2 g), sodium acetate (173 mg, 2.11 mmol) and PCC (924 mg, 4.22 mmol) were suspended in CH_2Cl_2 (20 mL). The oxidation mixture was cooled by means of an ice bath, and 2-*endo*-hydroxy-4-*exo*-chloro-7-*endo*-carbomethoxy-*cis*-bicyclo[3.3.0]octane (**24**) (455 mg, 2.11 mmol), dissolved in CH_2Cl_2 (1 mL) was added at once. The mixture was stirred for 72 hours at room temperature. Usual working-up yielded 300.6 mg (79%) of **27**. ^1H NMR (400 MHz) δ 7.53 (dd, J_1 5.6,J_2 2,7 Hz, 1H, H_4), 5.97 (dd, J_1 5.6, J_2 1.9 Hz, 1H, H_3), 3.56 (s, 3H, CH_3), 3.31 - 3.5 (m, W/2 25 Hz,1H, H_5), 2.88 (quintet, J 6.75 Hz, 1H, H_7), 2.78 (dt, J_1 8.9,J_2 6,6 Hz, 1H, H_1), 2.05 - 2.28 (m, 3H, H_{6exo} and $8_{exo,endo}$), 1.92 (dt, J_1 13,J_2 5,7 Hz, , 1H, H_{6endo}). ^{13}C NMR (25.3 MHz, $CDCl_3$) δ 211.2 (C_2O), 173.8 (CO-ester), 166.3 (C_4), 132.0 (C_3), 51.5 (CH_3), 48.6 (C_7), 46.3, 44.8, (2xCH), 32.1 (C_6), 30.7 (C_8). Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.59; H, 6.72.

***cis-anti-cis*-2-Oxo-5-methylene-10-*endo*-carbomethoxytricyclo[6.3.0^{3,7}]undecane (28).**

7-*endo*-Carbomethoxy-*cis*-bicyclo[3.3.0]oct-3-en-2-one (**27**) (90 mg, 0.5 mmol) and [2-(acetoxymethyl)-3-allyl]trimethylsilane (130 mg, 0.7 mmol) were added under argon to a solution of $Pd(OAc)_2$ (8.8 mg, 0.04 mmol) and triisopropyl phosphate (58 mg, 0.28 mmol) in toluene (2 mL). The resulting mixture was heated to reflux for 18 h. The reaction was cooled and the solvent removed *in vacuo*. The crude product which contained about 10% of a second product, was purified by flash chromatography (pentane/ether = 75/25) to give 58.8 mg (50 %) of **28** as a colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 4.77 (dm, J_1 13.5 Hz, 2H, $=CH_2$), 3.59 (s, 3H, CH_3), 2.4 - 2.85 (m, 8H), 2.17-2.28 (m, 2H), 1.88 - 1.98 (m, 2H), 1.51 (dt, J_1 = 13J_2 = 10.4 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 223.3 (C_2O), 175.1 (CO-ester), 150.1 (C_5), 106.7 (C_{12}), 51.8 (CH_3), 51.0 (C_{10}), 50.7, 46.6 (C_3 and C_1), 45.1, 43.9 (C_7 and C_8), 40.2, 37.0 (C_4 and C_6), 35.6 (C_9), 32.3 (C_{11}).

Di-μ-chloro-bis(2*exo*-chloro-5-*endo*-vinyl-3-norbornyl)dipalladium (31) and di-μ-chloro-bis(2*exo*-acetoxy-5-*endo*-vinyl-3-norbornyl)dipalladium (32a)[29]. Both complexes have been prepared according to Wipke and Goeke.

Oxidation of 31 and 32a with $CuCl_2$.

31 or **32a** (0.6 mmol), $CuCl_2$ (200 mg, 1.5 mmol) and NaOAc (80 mg, 1 mmol) were heated in HOAc (2.5 mL) at 80° C for 3h. The product was isolated in the way described for the catalytic cyclisation of *endo*-5-vinyl-2-norbornene (**2**). The cyclised products **4** and **5** were obtained in a ratio of 67:23, yield 70-80 mg (53-60%)

[Dipyridyl(2*exo*-acetoxy-5-*endo*-vinyl-3-*endo*-norbornyl)palladium] [BF_4] (34).

σ–π complex **32a**[29] (38 mg, 0.046 mmol) was added to a solution of $AgBF_4$ (18 mg, 0.092 mmol) in acetone (10 mL). After stirring (20-25 min) the yellow solution was filtered from AgCl and 2,2'-bipyridine (14 mg, 0.092 mmol) was added. The solution became colourless. Stirring was continued for 30 min and the solvent removed. Ether (10 mL) was added and the white product was filtered, washed with ether and air dried. Yield 57 mg (85%). For the X-ray structure determination the product has been recrystallized from acetonitrile.

^{1}H NMR (400 MHz, CD_3COCD_3) δ 8.36 (d, *J* 8.2 Hz, 4H), (t, *J* 7.9 Hz, 2H), 7.68 (dt, J_1 1.2 J_2 5.6 Hz, 2H), 6.10 (dd, J_1 15.2 J_2 8.1 Hz, 1H, H_8), 5.22 (dd, J_1 15.2 J_2 1.5 Hz, 1H, H_{10}), 5.07 (m, W/2 3 Hz, 1H, H_2), 4.88 (dd, J_1 8.2 J_2 1.7 Hz, 1H, H_9), 3.07 (m, W/2 9 Hz, 1H, H_4), 2.88 (t, *J* 3.5 Hz, small couplings, 1H, H_{3exo}), 2.68 (m, W/2 18 Hz, 1H, H_{5exo}), 2.40 (dq, J_1 4.9 J_2 1.4 Hz, 1H, H_1), 2.12 - 2.18 (m, partially hidden by acetone, 1H, H_{6exo}), 2.03 (s, 3H, OAc), 1.73 (ddd, part of an AB, J_1 13.1 J_2 4.3 J_3 2.3 Hz, 1H, H_{6endo}), 1.62 (d, part of an AB, J_1 10.3 Hz, small couplings, 1H, H_{7syn}), 1.42 (dq, part of an AB, J_1 10.4 J_2 1.5 Hz, 1H, H_{7anti}). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.9 (CO), 150.3 (C_{arom}), 142.2 (C_{arom}), 128.3 (CH_{arom}), 124.6 (CH_{arom}), 120.1 (C_8), 118,3 (CH_{arom}), 85.3 (C_9), 80.9 (C_2), 60.6 (C_3), 47.4 (C_4), 43.3 (C_5), 43.0 (C_1), 34.1 (C_7), 33.2 (C_6), 21.5 (CH_3).

X-ray data collection and structure solution of **34**

34 crystallized in the monoclinic space group $P2_1/c$, with a=10.370 (3), b=11.802 (4), c=17.089 (6) Å, 90/95.36(5)/90°; and V=2082 (2) Å^3; D_c=1.69 g cm3; M_r=452.17, Z=4, F(000) 1068, μ=9.33 cm^{-1}. A crystal of size 0,4 x 0,3 x 0,2 mm obtained from acetonitrile at 20°C was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a monochromator for Mo-K_α radiation (λ=0.71069 Å), θ_{max}=24°; ω/2θ scan, θmax = 24°, Δδ = 1.0 + 0.35tanθ°, at *T* = 298K, were used in the structure determination. The structure was determined by direct methods (MULTAN)[72] using SDP software[73] and completed by the difference Fourier method. H-atoms were introduced at idealized positions in the calculation before the last refinement cycles but not refined. Full least square refinement included isotropic thermal parameters for non H-atoms. A final difference Fourier synthesis did not reveal any peak of density > 0.35e Å^{-3}. *R* = 0.034 and R_W 0.061 for 3319 unique reflections with $I>3\sigma$ (I) $w=1/\sigma^2$ (σ= estimated standard deviation on intensity). The non-hydrogen atom coordinates are listed in Table 3. Lists of H-atom coordinates, structure factors, and a complete table of bond lengths and angles are available from the authors.

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