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Nucleophilic Additions to Tricyclodecadienone Epoxides. The Payne Rearrangement of α,β-Epoxycyclopentanols Contained in a Rigid Tricyclic System

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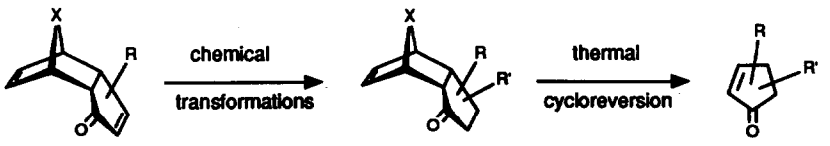
***Abstract**: Organometallic reagents add regio- and stereoselectively from the* convex exo*-face to the carbonyl function of* exo*-4,5-epoxytricyclodecenones* **5** *and* **8** *to give tricyclic* exo*-epoxy-*endo*-alcohols* **6** *and* **9**, *respectively. These initial adducts can undergo a Payne rearrangement to give inverted* endo*-epoxy-*exo*-alcohols* **7** *and* **10**, *respectively. The rearrangement is dependent on substrate, experimental conditions and type of organometallic reagent. Reduction of* **6** *and* **7** *with lithium aluminum hydride yields the same tricyclic* trans*-1,3-diols* **20**. *It is shown that reduction of* **6** *with lithium aluminum hydride proceeds via slow Payne rearrangement of its alkoxide* **11b** *to inverted alkoxide* **12b**, *followed by rapid addition of hydride to* C_4 *from the* exo*-face.*

INTRODUCTION

The use of *endo-* and *exo*-tricyclodecadienones **1** as synthetic equivalents for cyclopentadienones in the stereo- and enantioselective synthesis of cyclopentenoid natural products is well documented[1]. The steric restrictions imposed by the tricyclic framework ensure that reagents add to the enone moiety in **1** stereoselectively from the *convex exo*-face[1,2]. Cycloreversion of the functionalized tricyclodecenones by flash vacuum thermolysis (FVT) leads to stereochemically well-defined cyclopent-2-en-1-ones **2** (Scheme 1). In

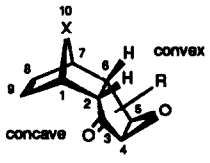
Scheme 1



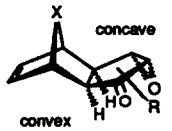
endo-**1** (X= CH_2)
exo-**1** (X= CH_2, O)

2

order to obtain access to oxygenated cyclopentenones, tricyclic epoxy ketones 3 and 4 were prepared by regio- and stereoselective epoxidation of the enone moiety in *endo*- and *exo*-1, respectively, by treatment with hydrogen peroxide in alkaline medium. These epoxy ketones were successfully used in the synthesis of *cis*- and *trans*-4,5-dihydroxycyclopent-2-en-1-ones, such as terrein[1a,c], pentenomycin[1b] and *epi*-pentenomycin[1d,f]. To broaden the synthetic applicability of these tricyclic epoxides, we studied the nucleophilic addition of metal hydrides and organometallic reagents to both *endo*- and *exo*-tricyclodecadienone epoxides 3 and 4 (X= CH_2, R= H). These tricyclic epoxy ketones possess a carbonyl and an epoxy function and, therefore, reaction



3
(endo, X= CH_2)



4
(exo, X= CH_2, O)

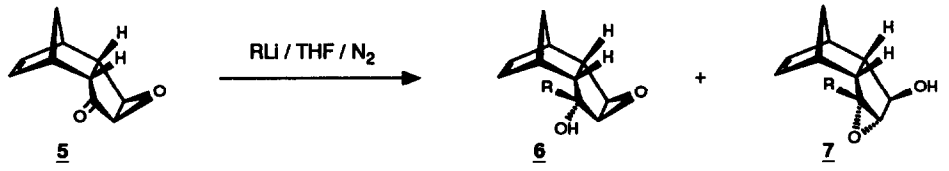
may occur at either functionality. A main factor determining the chemo- and stereoselectivity of nucleophilic additions to these rigid tricyclic epoxy ketones is the accessibility of the respective electrophilic centers. Nucleophilic additions to the ketone function in 3 from the *concave* face will on one hand be sterically hindered by the C_8-C_9 double bond, while on the other hand approach from the *convex* face of the molecule may experience serious interference of the epoxide function. A similar situation is encountered in *exo*-tricyclodecadienone epoxide 4 (X= CH_2), where the *concave* face is shielded by H_{syn} of the C_{10} methylene bridge. In this paper, we report on the chemo- and stereoselective reaction of metal hydrides and organometallics with the *exo*-epoxytricyclodecenones 5 (*i.e.* 3 (X= CH_2, R= H)) and 8 (*i.e.* 4 (X= CH_2, R= H))[2,3].

ADDITION OF ORGANOMETALLICS TO *EXO*-4,5-EPOXYTRICYCLODECENONES

Results

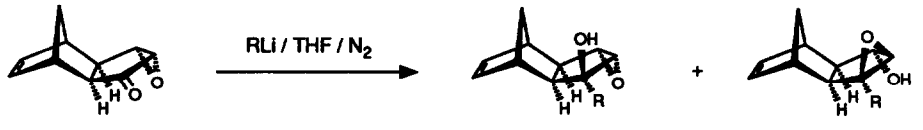
In order to establish the steric and electronic factors that determine the chemo- and stereoselectivity of

Scheme 2



5 6 7

Scheme 3



8 9 10

Table 1. Addition of Metal Hydrides and Organometallics to *exo*-4,5-Epoxy-*endo*-tricyclodecenone 5.

entry	reagent	product composition [a]		ΔE [b]
1	$LiAlH_4$	100% 6a	---- 7a [c]	+ 1.0
2	$NaBH_4$	84% 6a	16% 7a	+ 1.0
3	MeLi	86% 6b	14% 7b	+ 2.0
4	*n*-BuLi	70% 6c	30% 7c	+ 2.5
5	*s*-BuLi	24% 6d [d]	76% 7d [d]	+4.4/5.1 [e]
6	*t*-BuLi	---- 6e [c]	100% 7e	+ 5.6
7	PhLi	100% 6f	---- 7f [c]	+ 5.0

[a] by capillary GC of the crude mixture after one hour, except entries 1 (3 hours) and 2 (3 days); [b] (MM2-energy of 11) - (MM2-energy of 12) in kcal/mol; [c] not found; [d] 1:1.3 mixture of two diastereomers with R- resp. S-configuration at the stereogenic center of the *s*-Bu substituent; [e] R- and S-configuration on *sec*-butyl group.

Table 2. Addition of Metal Hydrides and Organometallics to *exo*-4,5-Epoxy-*exo*-tricyclodecenone 8.

entry	reagent	product composition [a]		ΔE [b]
1	$LiAlH_4$	65% 9a	28% 10a [c]	- 1.5
2	$NaBH_4$	71% 9a	29% 10a	- 1.5
3	MeLi	100% 9b	---- 10b [d]	+ 1.2
4	*n*-BuLi	---- 9c [d]	100% 10c	+ 1.6
5	*s*-BuLi	---- 9d [d]	100% 10d [e]	+ 3.4/4.0 [f]
6	*t*-BuLi	---- 9e [d]	100% 10e	+ 3.8
7	PhLi	74% 9f	26% 10f	+ 3.8

[a] by capillary GC of the crude mixture after one hour, except entry 2 (3 days); [b] (MM2-energy of 13) - (MM2-energy of 14) in kcal/mol; [c] 7% 21a; [d] not found; [e] 1:1.4 mixture of two diastereomers with R- resp. S-configuration at the stereogenic center of the *s*-Bu substituent; [f] R- and S-configuration on *sec*-butyl group.

nucleophilic additions to *exo*-4,5-epoxy-*endo*-tricyclodecenone 5 and *exo*-4,5-epoxy-*exo*-tricyclodecenone 8, reactions with a selection of metal hydrides and organolithium reagents with different steric and electronic properties, *viz.* $NaBH_4$, $LiAlH_4$, MeLi, *n*-BuLi, *s*-BuLi, *t*-BuLi and PhLi were investigated.

Reaction of 5 and 8, under standard conditions (*cf.* experimental section; tetrahydrofuran, N_2, 1 hour), with both metal hydrides and the organolithium reagents gave in all cases one or two α,β-epoxy alcohols (Schemes 2 and 3 and Tables 1 and 2)[4]. Isolated yields were excellent (>80%), but loss of some alcoholic

product had to be accepted during purification by flash chromatography. Based on their spectral data (*vide infra*) the products were assigned structures **6**, **7**, **9** and **10**, respectively. Monitoring the product formation by cap. GC revealed that the *exo*-epoxy-*endo*-alcohols **6** and **9**, respectively, were the initial products in all cases, irrespective of reagent or substrate used. No products resulting from addition from the *concave endo*-face in **5** or **8** were found, showing that the initial addition step occurs chemo- and stereoselectively at the *convex exo*-face of the carbonyl function. The formation of the inverted *endo*-epoxy-*exo*-alcohols **7** and **10**, respectively, is related to both the nature of the applied nucleophilic reagent and the configuration of the tricyclic epoxy ketone used. Starting from *endo*-tricyclodecenone epoxide **5** complete inversion of initially formed **6** was only observed when *t*-butyllithium was used. In all other cases only partial inversion took place when the mixture was stirred for one hour (Table 1). For the reactions of *exo*-tricyclodecenone epoxide **8** complete inversion was observed for all butyllithium reagents (Table 2). Comparison of the experimental data collected in tables 1 and 2 indicates that (i) increasing the steric bulk of the alkyl group R leads to an increase in the formation of inverted epoxy alcohols and (ii) *exo*-epoxy-*endo*-alcohols **9**, derived from *exo*-tricyclodecenone epoxide **8**, undergo a more efficient rearrangement to isomeric *endo*-epoxy-*exo*alcohols than the *exo*-epoxy-*endo*-alcohols **6**, derived from *endo*-tricyclodecenone epoxide **5**. Remarkably, addition of phenyllithium to **5** did not lead to any significant formation of inverted epoxy alcohol **7f**, whereas for **8** partial formation of **10f** was observed.

The use of extreme long reaction times did generally not lead to other products or complicated mixtures. Only for the reduction of **5** and **8** with lithium aluminum hydride, formation of a third reaction product was observed after more than 3-4 days and using 5-10 equiv. of hydride (*vide infra*).

Structural assignments

On the basis of their spectral data, the secondary products were identified as inverted *endo*-epoxy-*exo*-alcohols **7** and **10**, respectively. In particular the presence of a resonance at *ca.* 3.8 ppm in the ^{1}H-NMR spectra of **7b-f** and **10b-f**, which is typical for a methine proton in a -C(H)OH- moiety, allows unambiguous distinction between these inverted epoxy alcohols and their non-inverted analogs **6b-f** and **9b-f**, respectively. For the reduction products **6a** and **7a**, differentiation of the isomeric products was accomplished on the basis of the coupling constants between H_2 and H_3. According to the Karplus rule, $J_{2,3}$ is expected to be larger for **6a** than for the inverted epoxy alcohol **7a**, because for **6a** protons H_2 and H_3 are in a fixed *cis*-configuration, whereas for **7a** the comparable protons are in a fixed *trans*-configuration. The same holds for a comparison between structure **9a** and **10a**. The expected difference in coupling constants was indeed observed, *viz.* $J_{2,3}$(**6a**)=7.6 Hz, $J_{2,3}$(**7a**)=2.2 Hz, $J_{2,3}$(**9a**)=7.8 Hz and $J_{2,3}$(**10a**)=3.8 Hz.

Discussion

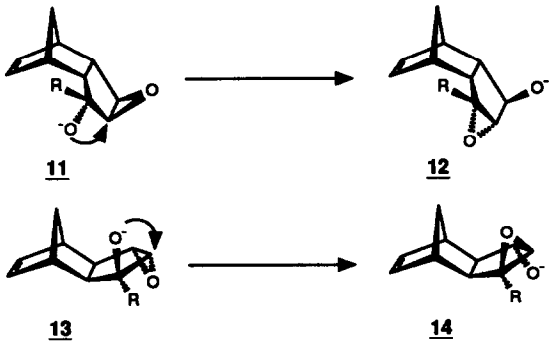
The exclusive formation of *endo*-alcohols **6** and **9** as the initial addition products clearly demonstrates that nucleophilic addition of such reactive species as organolithium compounds to tricyclodecenone epoxides **5** and **8** is solely determined by the steric impact of the norbornene moiety. Apparently, the *exo*-4,5-epoxide function does not hamper this nucleophilic attack from the *convex* face. In this respect the stereochemical pathway observed for nucleophilic additions to both tricyclic epoxides **5** and **8** conforms to that observed for nucleophilic additions to the corresponding parent tricyclodecadienones[2a].

THE PAYNE REARRANGEMENT

Mechanistic considerations

The formation of *endo*-epoxy-*exo*-alcohols 7 and 10 as secondary reaction products upon addition of metal hydrides or organolithium compounds to 5 and 8, respectively, can be explained by assuming an intramolecular epoxide ring opening of the initially formed *endo*-alkoxide anions 11 and 13, to give *exo*-alkoxide anions 12 and 14, respectively (Scheme 4). Such an epoxide migration or Payne rearrangement[5]

Scheme 4



11 12 13 14

is well documented for acyclic epoxy alcohols, but has not yet been described for α,β-epoxy cyclopentanols. The product ratio of such rearrangements is generally assumed to be determined by the relative stabilities of the isomeric α,β-epoxy alkoxides. Therefore, steric and electronic factors should have a significant effect on the ratios 6:7 and 9:10. In the initially formed *exo*-epoxy-*endo*-alcohols 6 and 9, the newly introduced R is in a sterically unfavorable eclipsed conformation with respect to the epoxide function. MM2-Calculations[6,7] confirm that steric congestion in inverted products 7 and 10 is considerably less than in 6 and 9, and therefore *endo*-epoxy-*exo*-alcohols 7 and 10 are thermodynamically more stable than *exo*-epoxy-*endo*-alcohols 6 and 9, respectively (Tables 1 and 2). Formation of *endo*-epoxy-*exo*-alcohols 7 and 10 is, for R≠H, also electronically favored as secondary alkoxides are generally more stable than tertiary ones. Both considerations are in agreement with the observed increase in the amount of inverted *endo*-epoxy-*exo*-alcohols 7 and 10 with increasing steric volume of R.

In order to establish whether the observed Payne rearrangement of α,β-epoxy alcohols is an equilibrium, all four α,β-epoxy alcohols 6, 7, 9 and 10 were treated with lithium diisopropylamide to give their corresponding alcoholates 11, 12, 13 and 14. Of these alcoholates the *exo*-epoxy-*endo*-isomers, *viz.* 11 and 13, rearranged to 12 and 14, respectively, whereas *endo*-epoxy-*exo*-isomers 12 and 14 were stable under these conditions. This means that, although it stops at a certain ratio of inverted and non-inverted products, the Payne rearrangement is not an equilibrium. The reason for the rearrangement not to proceed beyond a certain point remains unclear at this moment.

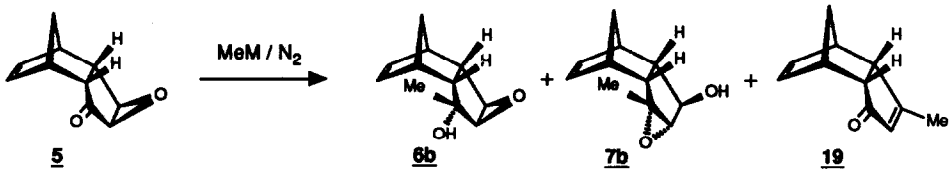
Manipulation of product ratios

From a synthetic point of view, product control in the nucleophilic additions to 5 and 8 is essential for future synthetic applications and therefore a more detailed study of the methylation of epoxy ketone 5, was

undertaken.

An important factor which could strongly affect product ratios in the Payne rearrangement is the nucleophilicity of the oxygen anion in alkoxides **11** and **13**. Strong aggregation or complexation with its positively charged counter ion, *e.g.* the lithium cation, will considerably decrease the nucleophilicity of this alkoxide anion and consequently lower the ease of intramolecular epoxide ring opening. Attempts to control the Payne rearrangement were therefore aimed at affecting the interaction between both ions, *e.g.* by changing the metal of the organometallic or by adding a salt to change the dielectric properties of the medium.

Table 3. Effect of the Reaction Medium on the Addition of Organometallics to **5**.



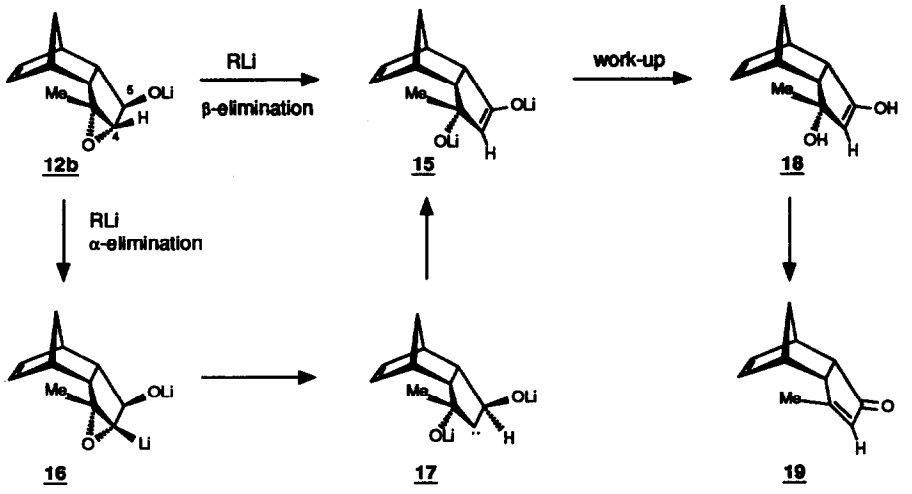
5 **6b** **7b** **19**

			product composition [b]		
solvent	reagent	time [a]	**6b**	**7b**	**19**
tetrahydrofuran	MeLi	4	47%	53%	---- [c]
ether	MeLi	10	49%	35%	16%
tetrahydrofuran / LiCl [d]	MeLi	4	57%	43%	---- [c]
tetrahydrofuran	MeMgI	3	---- [c]	100%	---- [c]

[a] in days; [b] relative yields as determined by cap. GC; [c] not formed; [d] 4 equiv.

Changing the solvent from tetrahydrofuran to ether altered the ratio of **6b**:**7b** only slightly, although it did affect the product composition. Besides **6b** and **7b** a third product, to which, on basis of spectral evidence and independent synthesis[1k], structure **19** was assigned, was isolated in low yield (Table 3). Scrutinizing this reaction showed that **19** is a secondary reaction product since it is definitely absent after the addition of methyllithium is complete. Its formation is explained by the well-documented[8] rearrangement of epoxides to allylic alcohols by treatment with organolithium bases. Although these rearrangements generally proceed via a *syn* β-elimination, *viz.* abstraction of H_{endo} at C_5 and formation of enolate **15**, a competitive α-elimination, *viz.* abstraction of H_{exo} at C_4 to yield **16**, formation of carbene **17** and finally a 1,2-hydrogen shift to enolate **15**, cannot be excluded. Because β-elimination requires deprotonation at C_5 from the sterically hindered *concave* face and because such a deprotonation will lead to an unstable 1,2-dianion intermediate, the rearrangement might even occur preferentially via α-elimination. For both routes, work-up of the reaction mixture will lead to enol **18** which, after ketonization, will rapidly eliminate water to form β-methyl-enone **19**. Convincing support for such an indirect mechanism comes from the observation that treatment of enantiopure (+)-**5** with methyllithium in ether gave only (-)-**19**. Based on the known absolute configurations of (+)-**5** and (-)-**19**[1k] this result unambiguously proves that the tricyclic skeleton has changed configuration during this reaction as the result of a formal 1,3-shift of the carbonyl function.

Scheme 5



Page *et al.*[5b] reported that the Payne rearrangement of α,β-epoxy alcohols is strongly affected by adding lithium chloride to the reaction mixture in tetrahydrofuran. They suggested that an increase of polarity of the solution would be responsible for this effect. In contrast to these observations, in the present case no significant change in the ratio of inverted and non-inverted products was found, when lithium chloride was added to the reaction mixture in various quantities, up to 4 equivalents.

Better results were obtained when methylmagnesium iodide was used instead of methyllithium. Under these conditions almost complete formation of inverted epoxy-alcohol **7b** was achieved[9].

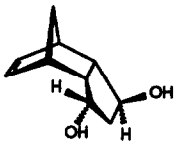
The different effect of methyllithium and methylmagnesium iodide on the amount of inversion in their reaction with **5** may be explained by their different Lewis acid character and the difference in nucleophilicity of the intermediate alkoxide anion bound to the respective metal cations. Being a stronger Lewis acid, methylmagnesium iodide is assumed to be superior in activating the epoxide function towards intramolecular nucleophilic opening as considerable complexation of the epoxy oxygen with the Grignard reagent may occur.

The results of the addition of an organozinc reagent to **5** in a recently published stereoselective synthesis of clavulones[1g], show, however, that the Lewis acidity of the organometallic reagent alone is not sufficient to explain the observed results. Whereas the addition of oct-2-ynyl magnesium bromide $BrMgCH_2C{\equiv}C(CH_2)_4CH_3$ to **5** gave a complex mixture of products containing the corresponding addition products **6** and **7** (R: $CH_2C{\equiv}C(CH_2)_4CH_3$), the addition of the less reactive zinc octynyl reagent, $BrZnCH_2C{\equiv}C(CH_2)_4CH_3$ leads to non-inverted epoxy alcohol **6** (R: $CH_2C{\equiv}C(CH_2)_4CH_3$) in almost quantitative yield. No inverted epoxy alcohol **7** (R: $CH_2C{\equiv}C(CH_2)_4CH_3$) was obtained at all, although the organozinc reagent is a superior Lewis acid compared to the organomagnesium reagent.

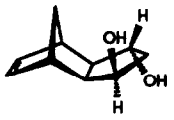
REDUCTION OF *EXO*-EPOXY-*ENDO*-ALCOHOLS

Reduction of exo-*epoxytricyclodecenones*

The reduction of tricyclodecenone epoxides **5** and **8** with lithium aluminum hydride in tetrahydrofuran is a fast process leading to initial formation of epoxy alcohols **6a** and **9a**, respectively. Only after prolonged reaction times these alcohols slowly rearrange to **7a** and **10a**, respectively (Tables 1 and 2). During this process, in both cases, the formation of a third product was observed, which was only isolated for the reduction of **8**. Based on its spectral data, this product was tentatively assigned 1,3-diol structure **21a**. By



20a



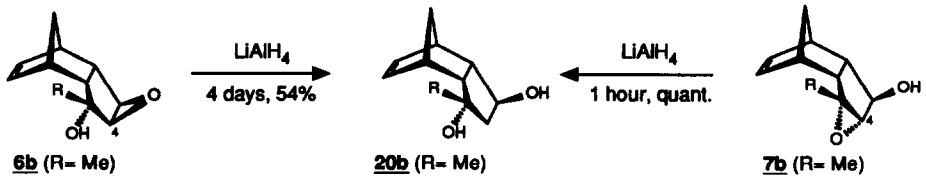
21a

analogy we assume that the tertiary product in the reaction of **5** with lithium aluminum hydride is 1,3-diol **20a**. The formation of these diols may be explained by rapid ring opening of the epoxide ring of **7a** and **10a** by hydride substitution at C_4, which is now readily accessible from the relatively unhindered *convex* face of the molecule. In order to study this latter reduction process in more detail and to secure its regio- and stereochemistry, we subjected both epoxy alcohols **6b** and **7b** to treatment with lithium aluminum hydride in tetrahydrofuran.

Reduction of epoxytricyclodecenols

On treatment with lithium aluminum hydride for four days, **6b** gave tricyclic diol **20b** in 54% yield together with 5% of **7b**. More than 40% of the starting material was still present after this long reaction time. Under identical conditions, reduction of inverted adduct **7b** was complete within 1 hour to give the same diol **20b** in quantitative yield (Scheme 6). The low reactivity of **6b** as compared to **7b** can be explained in two

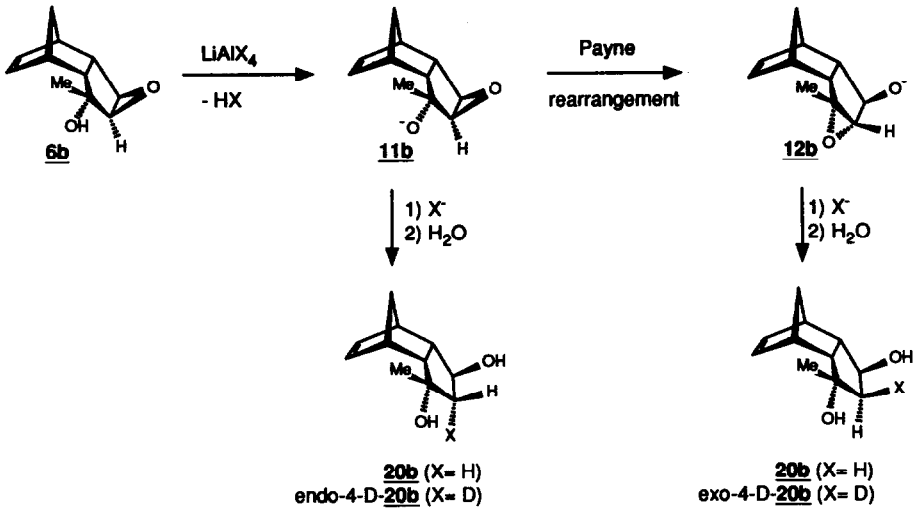
Scheme 6



6b (R= Me) **20b** (R= Me) **7b** (R= Me)

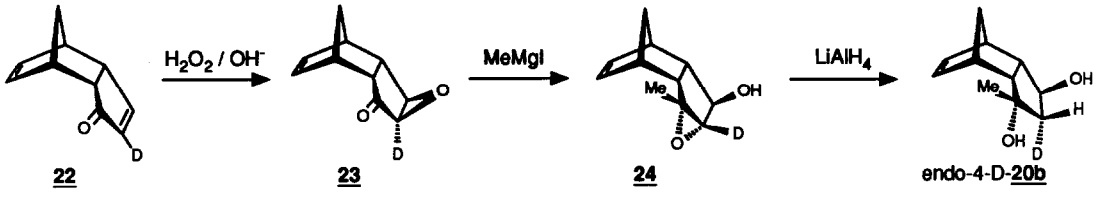
different ways (Scheme 7). Treatment of **6b** with lithium aluminum hydride will first yield non-inverted alkoxide anion **11b**. The necessary attachment of a hydrogen atom to C_4 can now occur by two pathways, *viz.* (i) slow, direct hydride substitution of the epoxide function at the sterically crowded *concave endo*-face in **11b** or (ii) first a slow Payne rearrangement to **12b**, followed by a fast hydride substitution of the epoxide function at the readily accessible *convex exo*-face. Both mechanisms eventually lead to tricyclic diol **20b** (X= H). Although the isolation of some inverted epoxide **7b** after reduction of **6b** with lithium aluminum hydride strongly supports the latter mechanism, unambiguous prove for this pathway was obtained from a deuterium labeling experiment. From scheme 7 it can be deduced that when **6b** is treated with lithium aluminum

Scheme 7



deuteride each mechanism will give a diol with different stereochemistry for the deuterium atom at C_4. Direct substitution will lead to *endo*-4-D-**20b**, whereas Payne rearrangement followed by epoxide substitution will give *exo*-4-D-**20b**. When **6b** was treated with lithium aluminum deuteride for one day[11], formation of a single deuterated diol was observed, whose spectral data were entirely identical to those obtained for the product arising from reduction of inverted epoxide **7b** with lithium aluminum deuteride, *i.e. exo*-4-D-**20b**. In order to unequivocally establish the position of the deuterium atom in *exo*-4-D-**20b**, C_4-deuterated *endo*-epoxy alcohol **24** was synthesized independently, starting from C_4-deuterated tricyclodecadienone **22**[10] (Scheme 8). Owing

Scheme 8

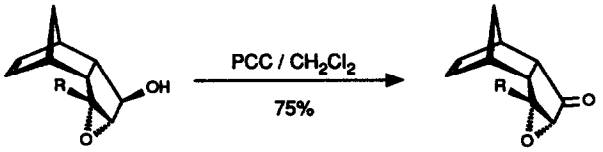


to the well-established stereochemistry of all conversions leading to deuterated *endo*-epoxy-*exo*-alcohol **24** the configuration of the deuterium atom in this compound is definitely *exo*. The product isolated from reduction of **24** with lithium aluminum hydride (*i.e. endo*-4-D-**20b**), exhibited a different ^{1}H-NMR spectrum as compared with *exo*-4-D-**20b**. Therefore, it may be concluded that reduction of non-inverted epoxy alcohol **6b** to diol **20b** does not proceed through direct substitution at the epoxide function in **6b** but involves an initial Payne rearrangement of its alkoxide **11b** to **12b**, followed by regio- and stereoselective epoxide ring opening at C_4 in **12b**.

SYNTHESIS OF *ENDO*-4,5-EPOXY-*ENDO*-TRICYCLODECENONES

Having attained good access to *endo*-epoxy-*exo*-alcohols 7, conversion of these alcohols in the corresponding *endo*-epoxy ketones 25, was considered (Scheme 9). These *endo*-epoxy ketones are

Scheme 9



7b R= Me 25b R= Me

synthetically interesting compounds as they, in contrast to *exo*-epoxy ketones 3, contain an epoxide function which is readily accessible from the *convex* face and therefore can probably be conveniently substituted with a great variety of nucleophiles. Oxidation of 7b with pyridinium chlorochromate proceeded smoothly to give *endo*-4,5-epoxytricyclodecenone 25b in 75% yield.

CONCLUDING REMARKS

Metal hydrides and organolithium reagents add regio- and stereoselectively from the *convex exo*-face to the carbonyl function of parent *exo*-epoxytricyclodecenones 5 and 8. The initial adducts, *viz.* *exo*-epoxy-*endo*-alcohols 6 and 9, can undergo an irreversible Payne rearrangement to give inverted *endo*-epoxy-*exo*-alcohols 7 and 10, respectively. It was found that the product ratio is dependent on both the nature of the nucleophile and the reaction conditions. By using Grignard reagents instead of organolithium compounds complete formation of inverted *endo*-epoxy-*exo*-alcohols 7 was achieved.

Reduction of *exo*-epoxy-*endo*-alcohols 6 and *endo*-epoxy-*exo*-alcohols 7 with lithium aluminum hydride both give *trans*-1,3-diols 20. Deuterium labelling showed that reduction of 6 to 1,3-diol 20 proceeds via a slow Payne rearrangement of alkoxide 11 to inverted alkoxide 12, followed by fast hydride substitution at C_4 of the *endo*-epoxide function.

EXPERIMENTAL SECTION

General remarks

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were taken on a Perkin Elmer 298 infrared spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AM-400, using TMS as an internal standard. For mass spectra a double focussing VG 7070E mass spectrometer was used. Flash chromatography was carried out at a pressure of *ca.* 1.5 bar, a column length of 15-25 cm and a column diameter of 1-4 cm, using Merck Kieselgel 60H, unless stated otherwise. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O 1108 Elemental Analyzer. All solvents used were dried and distilled according to standard procedures.

General procedures

A: Reactions of exo-epoxytricyclodecenones 5 and 8 with metal hydrides and organometallic reagents

Approximately 1 mmol of starting material is dissolved in 10 ml of dry ether or tetrahydrofuran and at 0 °C and under a nitrogen atmosphere, 2 mmol of organometallic reagent is added. The resulting mixture is

stirred for 15 min. at 0 °C and subsequently at room temperature. The crude mixture is quenched with saturated aqueous ammonium chloride and then extracted with ether. The combined organic fractions are dried ($MgSO_4$), filtered and the solvent is removed under reduced pressure, to give the crude product. Analytical samples are obtained by flash chromatography and/or crystallization.

B: Reduction of epoxy alcohols **6b**, **7b** *and* **24** *with lithium aluminum hydride and lithium aluminum deuteride*

Tricyclic epoxy alcohol is dissolved in 10 ml dry tetrahydrofuran. A solution of lithium aluminum hydride in tetrahydrofuran (1 g/ 100 ml) is added at 0 °C and under a nitrogen atmosphere. The resulting mixture is stirred for 15 min. at 0 °C and subsequently at room temperature. The reaction is monitored by cap. GC and the crude mixture is quenched with saturated aqueous ammonium chloride. The organic fraction is separated, washed with water and the aqueous phases are extracted with ethyl acetate (3x). The combined organic fractions are dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to yield the crude product. Analytical samples are obtained by flash chromatography and/or crystallization.

exo-4,5-*Epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **5**

Epoxidation of *endo*-tricyclodecadienone *endo*-**1** (7.2 g, 50 mmol), following the procedure described by Chapmann and Hess[13] gave, after work-up, 7.2 g (88%) **5** as a sticky, white solid (95% pure, cap. GC). An analytical sample was obtained by crystallization. The compound is best stored in a nitrogen atmosphere, as its norbornene double bond is easily epoxidized by molecular oxygen.

5: white powder (*n*-pentane). m.p.: 135-140 °C. [Lit.[13] m.p.: 136-139 °C]. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.08 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$=2.5 Hz, 1H, H_9), 6.03 B of AB (dd, $J_{7,8}$=2.8 Hz, 1H, H_8), 3.58 (t, $J_{4,5}\approx J_{5,6}\approx$1.9 Hz, 1H, H_5), 3.25-3.23 (m, 1H, H_7), 3.22 (d, 1H, H_4), 3.11 (bs, 1H, H_1), 3.09 (t, $J_{1,2}\approx$4.1 Hz, 1H, H_2), 2.77 (ddd, $J_{2,6}$=6.5 Hz, $J_{6,7}$=4.6 Hz, 1H, H_6), 1.62 A of AB (dt, $J_{10a,10s}$=8.6 Hz, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10s}\approx J_{7,10s}\approx$1.5 Hz, 1H, H_{10s} or H_{10a}), 1.46 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3040-2820 (C-H, unsat. and sat.), 1735 (C=O) cm^{-1}. EI/MS: *m/e* (%) 162 (12,M^+), 97 (82,-C_5H_5), 66 (100,$C_5H_6^+$). Found: C 73.91, H 6.13 (calc. for $C_{10}H_{10}O_2$: C 74.06, H 6.21).

exo-4,5-*Epoxy*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **8**

Epoxidation of *exo*-tricyclodecadienone *exo*-**1** (6.1 g, 42 mmol), following the procedure described by Chapmann and Hess[13] gave, after work-up, 6.2 g (91%) **8** as a yellow oil (98% pure, cap. GC), which slowly crystallized. An analytical sample was obtained by crystallization. The compound is best stored in a nitrogen atmosphere, as its norbornene double bond is easily epoxidized by molecular oxygen.

8: white powder (*n*-pentane). m.p.: 35-36 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.29 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.22 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 3.71 (t, $J_{4,5}\approx J_{5,6}\approx$1.9 Hz, 1H, H_5), 3.55 (dd, $J_{4,6}$=0.9 Hz (W-coupling), 1H, H_4), 3.06 (bs, 1H, H_1 or H_7), 2.98 (bs, 1H, H_1 or H_7), 2.49 A of AB (d, $J_{2,6}$=6.3 Hz, 1H, H_2), 2.16 B of AB (dq, $J_{6,7}\approx$1.5 Hz, 1H, H_6), 1.40 A of AB (dt, $J_{10a,10s}$=9.4 Hz, $J_{2,10a}\approx J_{6,10s}\approx$1.7 Hz, 1H, H_{10a}), 1.30 B of AB (d, 1H, H_{10s}). IR ($CHCl_3$): υ 3080-2840 (C-H, unsat. and sat.), 1735 (C=O) cm^{-1}. EI/MS: *m/e* (%) 162 (2,M^+), 97 (21,-C_5H_5), 66 (100,$C_5H_6^+$). Found: C 73.63, H 6.18 (calc. for $C_{10}H_{10}O_2$: C 74.06, H 6.21).

exo-4,5-*Epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **6a** *and* endo-4,5-*epoxy*-endo-*tricyclo*-[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **7a**

Following general procedure A [tetrahydrofuran (10 ml), $NaBH_4$ (144 mg, 3.8 mmol), 3 days], **5** (168 mg, 1.0 mmol), gave, after work-up, a crude mixture consisting of 84% **6a** and 16% **7a** (cap. GC). After flash chromatography (*n*-hexane:ethyl acetate = 1:1), 129 mg (79%) **6a** was obtained as a white solid and 19 mg (12%) **7a** as a colorless oil. An analytical sample of **6a** was obtained by crystallization.

Following general procedure A [tetrahydrofuran (10 ml), $LiAlH_4$ (112 mg, 3.0 mmol), 3 h], **5** (96 mg, 0.59 mmol), gave, after work-up, pure **6a** (cap. GC).

6a: white needles (petroleum-ether 40-60). m.p.: 115-117 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.25 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.4 Hz, 1H, H_8 or H_9), 6.10 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 4.24 (d, $J_{2,3}$=7.6 Hz, 1H, H_3), 3.23 A of AB (d, $J_{4,5}$=2.1 Hz, 1H, H_4 or H_5), 3.21 B of AB (d, 1H, H_4 or H_5), 2.96 (bs, 2H, H_1 and H_7), 2.94 (dt, J=7.5 Hz and 3.8 Hz, 1H, H_2 or H_6), 2.85 (dd, J=7.5 Hz and 4.3 Hz, 1H, H_2 or H_6), 1.64 (bs, 1H, OH), 1.51 A of AB (bd, $J_{10a,10s}$=8.3 Hz, 1H, H_{10a} or H_{10s}), 1.37 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3720-3100 (H-bonded OH), 3600 (free OH), 3100-2820 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 164 (18,M^+), 147 (7,-OH), 98 (54,-C_5H_6), 81 (24,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 164.0835 (calc. for $C_{10}H_{12}O_2$ (M^+): 164.0837).

7a: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.14-6.09 (m, 2H, H_8 and H_9), 3.81 (t, $J_{2,3}\approx J_{3,4}\approx$2.2 Hz, 1H, H_3), 3.45 (t, $J_{4,5}\approx$2.4 Hz, 1H, H_4), 3.30 (d, 1H, H_5), 3.05 (bs, 1H, H_1 or H_7), 3.01 A of AB (dd, $J_{2,6}$=7.6 Hz, $J_{6,7}$=4.1 Hz, 1H, H_6), 2.92 (bs, 1H, H_1 or H_7), 2.29 B of AB (ddd, $J_{1,2}\approx$4.3 Hz, 1H, H_2), 2.17

(bs, 1H, OH), 1.49 A of AB (dt, $J_{10a,10s}$=8.4 Hz, J=1.8 Hz, 1H, H_{10a} or H_{10s}), 1.33 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3640-3080 (H-bonded OH), 3560 (free OH), 3080-2820 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 164 (1,M^+), 98 (15,-C_5H_6), 81 (13,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 164.0835 (calc. for $C_{10}H_{12}O_2$ (M^+): 164.0837).

exo-4,5-*Epoxy*-exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **6b** *and* endo-4,5-*epoxy*-exo-5-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **7b**

Following general procedure A [tetrahydrofuran (10 ml), 1.6 M MeLi in hexane (1.25 ml, 2.0 mmol), 1 h], **5** (159 mg, 1.0 mmol), gave, after work-up, a crude mixture consisting of 86% **6b** and 14% **7b** (cap. GC). After flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1), **6b** was obtained as a white solid and 19 mg (11%) **7b** as white needles. An analytical sample of **6b** (120 mg, 67%) was obtained by crystallization.

6b: white needles (petroleum-ether 40-60). m.p.: 104-106 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.16 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 3.16 A of AB (d, $J_{4,5}$=2.2 Hz, 1H, H_5), 3.08 B of AB (dd, $J_{4,6}$=0.7 Hz (W-coupling), 1H, H_4), 2.98 (bs, 1H, H_1 or H_7), 2.95 (bs, 1H, H_1 or H_7), 2.89 A of AB (ddd, $J_{2,6}$=7.8 Hz, $J_{6,7}$=4.4 Hz, 1H, H_6), 2.52 B of AB (dd, $J_{1,2}$=4.1 Hz, 1H, H_2), 1.55 (bs, 1H, OH), 1.49 A of AB (dt, $J_{10a,10s}$=8.2 Hz, J=1.8 Hz, 1H, H_{10a} or H_{10s}), 1.39 (s, 3H, -CH_3), 1.32 B of AB (dt, J=1.4 Hz, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3760-3100 (H-bonded OH), 3600 (free OH), 3100-2840 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 178 (24,M^+), 161 (77,-OH), 112 (75,-C_5H_6), 97 (27,-C_5H_6,-CH_3), 95 (100,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). Found: C 74.14, H 8.11 (calc. for $C_{11}H_{14}O_2$: C 74.13, H 7.92).

7b: white needles (petroleum-ether 40-60). m.p.: 105-107 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.20 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{7,8}$=3.1 Hz, 1H, H_8), 5.88 B of AB (dd, $J_{1,9}$=2.9 Hz, 1H, H_9), 3.77 (t, $J_{2,3}$=$J_{3,OH}$≈3.3 Hz, 1H, H_3), 3.02 (s, 1H, H_4), 2.98 A of AB (dt, $J_{2,6}$=10.5 Hz, $J_{1,2}$≈4.0 Hz, 1H, H_2), 2.93 (bs, 1H, H_7), 2.89 (bs, 1H, H_1), 2.79 B of AB (dd, $J_{6,7}$=3.5 Hz, 1H, H_6), 1.74 (bd, 1H, OH), 1.49 A of AB (dt, $J_{10a,10s}$=8.1 Hz, J=1.8 Hz, 1H, H_{10a} or H_{10s}), 1.43 (s, 3H, -CH_3), 1.34 B of AB (bd, 1H, H_{10a} or H_{10s}). IR ($CHCl_3$): υ 3720-3100 (H-bonded OH), 3600 (free OH), 3070 (C-H, unsat.), 3040-2800 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 178 (4,M^+), 160 (7,-H_2O), 112 (49,-C_5H_6), 97 (44,-C_5H_6,-CH_3), 95 (45,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). Found: C 73.79, H 7.72 (calc. for $C_{11}H_{14}O_2$: C 74.13, H 7.92).

exo-3-*n-Butyl*-exo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **6c** *and* exo-5-*n-butyl*-endo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **7c**

Following general procedure A [tetrahydrofuran (10 ml), 1.6 M *n*-BuLi in hexane (1.35 ml, 2.2 mmol), 1 h], **5** (142 mg, 0.88 mmol), gave, after work-up, a crude mixture consisting of 70% **6c** and 30% **7c** (cap. GC). After flash chromatography (*n*-hexane:ethyl acetate = 4:1), **6c** was obtained as a white solid and 64 mg (33%) **7c** as a colorless oil. An analytical sample of **6c** (100 mg, 52%) was obtained by crystallization.

6c: white needles (petroleum-ether 40-60). m.p.: 66-68 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.15 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 3.18 A of AB (d, $J_{4,5}$=2.2 Hz, 1H, H_5), 3.10 B of AB (dd, $J_{4,6}$=0.6 Hz (W-coupling), 1H, H_4), 2.94 (bs, 2H, H_1 and H_7), 2.85 A of AB (ddd, $J_{2,6}$=7.9 Hz, $J_{6,7}$=4.3 Hz, 1H, H_6), 2.52 B of AB (dd, $J_{1,2}$=4.0 Hz, 1H, H_2), 1.71-1.31 (m, 8H, -$(CH_2)_3CH_3$, H_{10a} and H_{10s}), 1.59 (bs, 1H, OH), 0.93 (t, $J_{CH2,CH3}$=7.3 Hz, 3H, -$(CH_2)_3CH_3$). IR (CH_2Cl_2): υ 3700-3070 (H-bonded OH), 3590 (free OH), 3040-2760 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (5,M^+), 202 (2,-H_2O), 154 (9,-C_5H_6), 137 (26,-C_5H_6,-OH), 97 (86,-C_5H_6,-*n*-Bu), 66 (100,$C_5H_6^+$), 57 (15,*n*-Bu^+). EI/HRMS *m/e*: 220.1467 (calc. for $C_{14}H_{20}O_2$ (M^+): 220.1463).

7c: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{7,8}$=3.0 Hz, 1H, H_8), 5.88 B of AB (dd, $J_{1,9}$=3.0 Hz, 1H, H_9), 3.77 (d, $J_{2,3}$=3.2 Hz, 1H, H_3), 3.01 (s, 1H, H_4), 2.97 A of AB (dt, $J_{2,6}$=10.5 Hz, $J_{1,2}$=4.1 Hz, 1H, H_2), 2.92 (bs, 1H, H_7), 2.89 (bs, 1H, H_1), 2.81 B of AB (dd, $J_{6,7}$=3.6 Hz, 1H, H_6), 1.85-1.31 (m, 8H, -$(CH_2)_3CH_3$, H_{10a} and H_{10s}), 1.55 (bs, 1H, OH), 0.91 (t, $J_{CH2,CH3}$=7.1 Hz, 3H, -$(CH_2)_3CH_3$). IR (CH_2Cl_2): υ 3740-3090 (H-bonded OH), 3600 (free OH), 3060 (C-H, unsat.), 3040-2780 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (30,M^+), 203 (87,-OH), 178 (27,-C_3H_6), 155 (72,-C_5H_5), 137 (100,-C_5H_6,-OH), 97 (59,-C_5H_6,-*n*-Bu), 66 (61,$C_5H_6^+$), 57 (27,*n*-Bu^+). EI/HRMS *m/e*: 220.1465 (calc. for $C_{14}H_{20}O_2$ (M^+): 220.1463).

exo-3-*sec-Butyl*-exo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **6d** *and* exo-5-*sec-butyl*-endo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **7d**

Following general procedure A [tetrahydrofuran (10 ml), 1.4 M *s*-BuLi in hexane (1.55 ml, 2.2 mmol), 1 h], **5** (171 mg, 1.1 mmol), gave, after work-up, a crude mixture consisting of 24% **6d** and 76% **7d** (cap. GC). After flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1), 57 mg (24%) **6d** was obtained as a white solid and 56 mg (23%) **7d** as a colorless oil. An analytical sample of **6d** (38 mg, 16%) was obtained by crystallization.

6d (1.3:1 mixture of two diastereomers, major isomer= **6d$_1$**, minor isomer= **6d$_2$**): white needles (petroleum-ether 40-60). m.p.: 64-69 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 2H, H_8 or H_9 of **6d$_1$** and **6d$_2$**), 6.13 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 2H, H_8 or H_9 of **6d$_1$** and **6d$_2$**), 3.21-3.20 A of AB (m, 2H, H_5 of **6d$_1$** and **6d$_2$**), 3.18 B of AB (d, $J_{4,5}$=2.2 Hz, 1H, H_4 of **6d$_2$**), 3.14 B of AB (d, $J_{4,5}$=2.2 Hz, 1H, H_4 of **6d$_1$**), 2.94 (bs, 2H, H_1 or H_7 of **6d$_1$** and **6d$_2$**), 2.87-2.83 (m, 4H, H_1 or H_7 and H_2 or H_6 of **6d$_1$** and **6d$_2$**), 2.60 B of AB (dd, $J_{2,6}$=7.9 Hz, $J_{1,2}$ resp. $J_{6,7}$=4.1 Hz, 2H, H_2 or H_6 of **6d$_1$** and **6d$_2$**), 1.77-1.13 (m, 12H -CH(CH$_3$)CH$_2$CH$_3$, H_{10a}, H_{10s} and OH, of **6d$_1$** and **6d$_2$**), 1.03 (d, $J_{CH,CH3}$=6.8 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **6d$_1$**), 0.99 (d, $J_{CH,CH3}$=6.9 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **6d$_2$**), 0.97 (t, $J_{CH2,CH3}$=7.3 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **6d$_1$**), 0.91 (t, $J_{CH2,CH3}$=7.4 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **6d$_2$**). IR (CH_2Cl_2): υ 3740-3100 (H-bonded OH), 3600 (free OH), 3060 (C-H, unsat.), 3040-2850 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (1,M$^+$), 154 (2,-C_5H_6), 137 (18,-C_5H_6,-OH), 97 (60,-C_5H_6,-*s*-Bu), 79 (11,-C_5H_6,-*s*-Bu,-H_2O), 66 (100,$C_5H_6^+$), 57 (37,*s*-Bu$^+$). EI/HRMS *m/e*: 220.1463 (calc. for $C_{14}H_{20}O_2$ (M$^+$): 220.1463).

7d: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): very complex, due to fast decomposition of this product to the *exo*-8,9-epoxide (by spontaneous epoxidation of the norbornene double bond by molecular oxygen[14]) and other, unidentified products. IR (CH_2Cl_2): υ 3740-3100 (H-bonded OH), 3600 (free OH), 3060 (C-H, unsat.), 3040-2770 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (4,M$^+$), 154 (15,-C_5H_6), 137 (63,-C_5H_6,-OH), 97 (74,-C_5H_6,-*s*-Bu), 79 (54,-C_5H_6,-*s*-Bu, -H_2O), 66 (100,$C_5H_6^+$), 57 (97,*s*-Bu$^+$). EI/HRMS *m/e*: 220.1465 (calc. for $C_{14}H_{20}O_2$ (M$^+$): 220.1463).

exo-5-*tert-Butyl*-endo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-exo-3-*ol* **7e**

Following general procedure A [tetrahydrofuran (10 ml), 1.7 M *t*-BuLi in hexane (1.20 ml, 2.0 mmol), 1 h], **5** (170 mg, 1.1 mmol), gave, after work-up, flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1) and crystallization an analytical sample of **7e** (97 mg, 40%). No **6e** was isolated.

7e: white needles (petroleum-ether 40-60). m.p.: 105-108 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{7,8}$=2.9 Hz, 1H, H_8), 5.87 B of AB (dd, $J_{1,9}$=2.8 Hz, 1H, H_9), 3.78 (d, $J_{2,3}$=2.9 Hz, 1H, H_3), 3.05 (s, 1H, H_4), 3.03 A of AB (dd, $J_{2,6}$=10.3 Hz, $J_{6,7}$=3.5 Hz, 1H, H_6), 2.92 B of AB (dt, $J_{1,2}$=3.8 Hz, 1H, H_2), 2.90 (bs, 2H, H_1 and H_7), 1.69 (bs, 1H, OH), 1.46 A of AB (dt, $J_{10a,10s}$=8.1 Hz, J= 1.7 Hz, 1H, H_{10a} or H_{10s}), 1.36 B of AB (d, 1H, H_{10a} or H_{10s}), 0.99 (s, 9H, -C(CH$_3$)$_3$). IR (CH_2Cl_2): υ 3720-3100 (H-bonded OH), 3600 (free OH), 3070 (C-H, unsat.), 3040-2780 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (9,M$^+$), 205 (25,-CH$_3$), 163 (28,-*t*-Bu), 154 (21,-C_5H_6), 137 (32,-C_5H_6,-OH), 97 (93,-C_5H_6,-*t*-Bu), 79 (33,-C_5H_6,-*t*-Bu,-H_2O), 66 (100,$C_5H_6^+$), 57 (80,*t*-Bu$^+$). Found: C 75.74, H 9.04 (calc. for $C_{14}H_{20}O_2$: C 76.33, H 9.15).

exo-4,5-*Epoxy*-exo-3-*phenyl*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-endo-3-*ol* **6f**

Following general procedure A [tetrahydrofuran (10 ml), 2.0 M PhLi in hexane (1.05 ml, 2.1 mmol), 1 h], **5** (170 mg, 1.1 mmol), gave, after work-up, flash chromatography (Al_2O_3, chloroform:benzene:ethyl acetate = 4:1:1) and crystallization an analytical sample of **6f** (131 mg, 50%). No **7f** was isolated.

6f: white plates (petroleum-ether 40-60). m.p.: 126.0-126.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (m, 2H, H_{ortho}), 7.38-7.35 (m, 2H, H_{meta}), 7.30-7.26 (m, 1H, H_{para}), 6.43 A of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.3 Hz, 1H, H_8 or H_9), 6.21 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.38 A of AB (dd, $J_{4,5}$=2.1 Hz, $J_{4,6}$=0.6 Hz (W-coupling), 1H, H_4), 3.32 B of AB (d, 1H, H_5), 3.12 and 3.06-3.02 (bs and m, 4H, H_1, H_2, H_6 and H_7), 1.93 (s, 1H, OH), 1.55 A of AB (dt, $J_{10a,10s}$=8.2 Hz, J=1.5 Hz, 1H, H_{10a} or H_{10s}), 1.40 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3700-3120 (H-bonded OH), 3580 (free OH), 3100-2780 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 240 (13,M$^+$), 222 (8,-H_2O), 174 (22,-C_5H_6), 157 (83,-C_5H_6,-OH), 146 (31,-C_6H_5,-OH), 105 (97, $C_6H_5C{\equiv}O^+$), 77 (55,$C_6H_5^+$), 66 (100,$C_5H_6^+$). Found: C 80.07, H 6.78 (calc. for $C_{16}H_{16}O_2$: C 79.97, H 6.71).

exo-4,5-*Epoxy*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-endo-3-*ol* **9a**, endo-4,5-*epoxy*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-exo-3-*ol* **10a** *and* exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-endo,exo-3,5-*diol* **21a**

Following general procedure A [tetrahydrofuran (10 ml), $NaBH_4$ (151 mg, 4.0 mmol), 3 days], **8** (176 mg, 1.1 mmol), gave, after work-up, a mixture consisting of 71% **9a** and 29% **10a** (cap. GC). After flash chromatography (*n*-hexane:ethyl acetate = 1:1), 82 mg (46%) **9a** and 32 mg (18%) **10a** were both obtained as colorless oils.

Following general procedure A [tetrahydrofuran (10 ml), $LiAlH_4$ (136 mg, 3.6 mmol)], **8** (177 mg, 1.1 mmol), gave, after one hour, a mixture of 65% **9a**, 28% **10a** and 7% **21a** (cap. GC). The reaction was continued for another three days to give, after work-up, a crude mixture consisting for 84% of **21a** (cap. GC). After flash chromatography (*n*-hexane:ethyl acetate = 1:1) and crystallization an analytical sample of **21a** was obtained as a white powder.

9a: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.21 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.12 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 4.32 (d, $J_{2,3}$=7.8 Hz, 1H, H_3), 3.50 A of AB (dd, $J_{4,5}$=2.2 Hz, $J_{4,6}$=0.9 Hz (W-coupling), 1H, H_4), 3.33 B of AB (d, 1H, H_5), 2.91 (bs, 1H, H_1

or H_7), 2.85 (bs, 1H, H_1 or H_7), 2.25 A of AB (dd, $J_{2,6}$=7.2 Hz, 1H, H_2), 2.20 B of AB (dt, $J_{7,6}\approx J_{2,6}$≈7.2 Hz, 1H, H_6), 1.81 (bs, 1H, OH), 1.56 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10s}), 1.42 B of AB (dt, $J_{2,10s}\approx J_{6,10s}$≈1.7 Hz, 1H, H_{10s}). IR (CH_2Cl_2): υ 3700-3100 (H-bonded OH), 3605 (free OH), 3080-2820 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 164 (1,M^+), 98 (9,-C_5H_6), 81 (30,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 164.0835 (calc. for $C_{10}H_{12}O_2$ (M^+): 164.0837).

10a: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.14 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.11 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.87 (bs, 1H, H_3), 3.72 A of AB (dd, $J_{3,4}\approx J_{4,5}$≈2.4 Hz, 1H, H_4), 3.39 B of AB (d, 1H, H_5), 2.80 (bs, 1H, H_1 or H_7), 2.75 (bs, 1H, H_1 or H_7), 2.36 A of AB (dd, $J_{2,6}$=6.7 Hz, J=0.7 Hz, 1H, H_2 or H_6), 2.08 (bs, 1H, OH), 1.64 B of AB (bdd, J=0.7 Hz, 1H, H_2 or H_6), 1.35 A of AB (dt, $J_{10a,10s}$=9.1 Hz, $J_{2,10s}\approx J_{6,10s}$=1.7 Hz, 1H, H_{10a}), 1.25 B of AB (d, 1H, H_{10s}). IR (CH_2Cl_2): υ 3700-3100 (H-bonded OH), 3570 (free OH), 3100-2820 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 164 (9, M^+), 98 (33,-C_5H_6), 81 (18,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 164.0837 (calc. for $C_{10}H_{12}O_2$ (M^+): 164.0837).

21a: white powder (petroleum-ether 40-60). ^{1}H-NMR (400 MHz, acetone-d_6): δ 6.13 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 6.10 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 4.33-4.28 (m, 1H, H_3 or H_5), 3.92-3.86 (m, 1H, H_3 or H_5), 3.65 (d, $J_{H,OH}$=4.8 Hz, 1H, -CH(OH)-), 3.54 (d, $J_{H,OH}$=3.8 Hz, 1H, -CH(OH)-), 2.77 (bs, 1H, H_1 or H_7), 2.67 (bs, 1H, H_1 or H_7), 2.09 A of AB (bt, $J_{2,6}\approx J_{2,3}$≈8.3 Hz, 1H, H_2), 2.01 A of AB (ddd, $J_{4n,4x}$=13.2 Hz, J_{cis}=6.0 Hz, J_{trans}=3.8 Hz, 1H, H_{4n} or H_{4x}), 1.91 B of AB (ddd, J_{cis} resp. J_{trans}=7.8 resp. 6.0 Hz, 1H, H_{4n} or H_{4x}), 1.84 (dd, $J_{5,6}$≈5.3 Hz, 1H, H_6), 1.67 A of AB (bd, $J_{10a,10s}$=8.6 Hz, 1H, H_{10a} or H_{10s}), 1.23 (bd, 1H, H_{10a} or H_{10s}). EI/MS: *m/e* (%) 166 (14,M^+), 149 (10,-OH), 130 (17,-$2H_2O$), 99 (100,-C_5H_7), 83 (55,-C_5H_6,-OH), 66 (100,$C_5H_6^+$).

exo-4,5-*Epoxy*-exo-3-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **9b**

Following general procedure A [tetrahydrofuran (10 ml), 1.6 M MeLi in hexane (1.30 ml, 2.1 mmol), 1 h], **8** (168 mg, 1.0 mmol), gave, after work-up, flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1) and crystallization, an analytical sample of **9b** (173 mg, 97%). No **10b** was isolated.

9b: white needles (petroleum-ether 40-60). m.p.: 71-73 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.18 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.08 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 3.34 A of AB (dd, $J_{4,5}$=2.2 Hz, $J_{4,6}$=0.7 Hz (W-coupling), 1H, H_4), 3.28 (d, 1H, H_5), 2.87 (bs, 1H, H_1 or H_7), 2.81 (bs, 1H, H_1 or H_7), 2.28 A of AB (dd, $J_{2,6}$=6.8 Hz, 1H, H_6), 1.77 B of AB (bd, 1H, H_2), 1.64 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10s}), 1.53 (s, 1H, OH), 1.42 (s, 3H, -CH_3), 1.41 (dt, $J_{2,10s}\approx J_{6,10s}$≈1.8 Hz, 1H, H_{10a}). IR (CH_2Cl_2): υ 3700-3120 (H-bonded OH), 3600 (free OH), 3080-2830 (C-H, unsat. and sat.) cm^{-1}. CI/MS: *m/e* (%) 179 (4,M+1$^+$), 161 (39,-H_2O), 112 (72,M^+-C_5H_6), 97 (38,M^+-C_5H_6,-CH_3), 95 (90,M^+-C_5H_6,-OH), 66 (100,$C_5H_6^+$). Found: C 74.41, H 7.97 (calc. for $C_{11}H_{14}O_2$: C 74.13, H 7.92).

exo-5-*n-Butyl*-endo-4,5-*epoxy*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **10c**

Following general procedure A [tetrahydrofuran (10 ml), 1.6 M *n*-BuLi in hexane (1.35 ml, 2.2 mmol), 1 h], **8** (175 mg, 1.1 mmol), gave, after work-up a crude mixture in near quantitative yield. After flash chromatography (*n*-hexane:ethyl acetate = 1:1), 85 mg (35%) **10c** was obtained as a colorless oil. No **9c** was isolated.

10c: colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.15-6.11 (m, 2H, H_8 and H_9), 3.83 (d, $J_{2,3}$=2.9 Hz, 1H, H_3), 3.22 (d, $J_{2,4}$=0.6 Hz (W-coupling), 1H, H_4), 2.80 (bs, 1H, H_1 or H_7), 2.72 (bs, 1H, H_1 or H_7), 2.27 A of AB (bd, $J_{2,6}$=9.2 Hz, 1H, H_2), 2.14 B of AB (d, 1H, H_6), 2.02 A of AB (d, $J_{10a,10s}$=8.5 Hz, 1H, H_{10s}), 1.93 (bs, 1H, OH), 1.84-1.77 and 1.72-1.65 (2m, 1H and 1H, -$CH_2(CH_2)_2CH_3$), 1.46-1.30 (m, 4H, -$CH_2(CH_2)_2CH_3$), 1.25 B of AB (dt, $J_{2,10a}\approx J_{6,10a}$≈1.5 Hz, 1H, H_{10a}), 0.93 (t, $J_{CH2,CH3}$=7.0 Hz, 3H, -$(CH_2)_3CH_3$). IR (CH_2Cl_2): υ 3720-3120 (H-bonded OH), 3595 (free OH), 3090-2800 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (1,M^+), 203 (2,-OH), 178 (9,-C_3H_6), 155 (88,-C_5H_5), 137 (54,-C_5H_6,-OH), 97 (80,-C_5H_6,-*n*-Bu), 66 (100,$C_5H_6^+$), 57 (21,*n*-Bu^+). EI/HRMS *m/e*: 220.1465 (calc. for $C_{14}H_{20}O_2$ (M^+): 220.1463).

exo-5-*sec-Butyl*-endo-4,5-*epoxy*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **10d**

Following general procedure A [tetrahydrofuran (10 ml), 1.4 M *s*-BuLi in hexane (1.55 ml, 2.2 mmol), 1 h], **8** (176 mg, 1.1 mmol), gave, after work-up, a crude mixture in near quantitative yield. After flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1), 113 mg (46%) **10d** was obtained as a colorless oil. No **9d** was isolated.

10d (1.4:1 mixture of two diastereomers, major isomer **10d$_1$**, minor isomer **10d$_2$**): colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.16-6.11 (m, 4H, H_8 and H_9 of **10d$_1$** and **10d$_2$**), 3.84 (d, $J_{2,3}$=3.5 Hz, 1H, H_3 of **10d$_2$**), 3.83 (d, $J_{2,3}$=3.1 Hz, 1H, H_3 of **10d$_1$**), 3.20 (d, $J_{2,4}$=0.7 Hz (W-coupling), 1H, H_4 of **10d$_2$**), 3.17 (d, $J_{2,4}$=0.7 Hz (W-coupling), 1H, H_4 of **10d$_1$**), 2.79 (bs, 2H, H_1 or H_7 of **10d$_1$** and **10d$_2$**), 2.72 (bs, 2H, H_1 or H_7 of **10d$_1$** and **10d$_2$**), 2.29 A of AB (bd, $J_{2,6}$=9.2 Hz, 1H, H_2 of **10d$_2$**), 2.26 A of AB (bd, $J_{2,6}$=9.3 Hz, 1H, H_2 of **10d$_1$**), 2.20 B of AB (dd, $J_{6,7}$≈1.1 Hz, 1H, H_6 of **10d$_1$**), 2.17 B of AB (dd, $J_{6,7}$≈1.0 Hz, 1H, H_6 of **10d$_2$**), 2.02-1.98 (m, 2H, H_{10s} of **10d$_1$** and **10d$_2$**), 1.78 (bs, 2H, OH of **10d$_1$** and **10d$_2$**), 1.68-1.24 (m,

8H, -CH(CH$_3$)CH$_2$CH$_3$ and H$_{10a}$ of **10d$_1$** and **10d$_2$**), 1.04 (d, $J_{CH,CH3}$=6.8 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **10d$_2$**), 1.03 (d, $J_{CH,CH3}$=6.9 Hz, 3H, -CH(CH$_3$)CH$_2$CH$_3$ of **10d$_1$**), 0.95 (t, $J_{CH2,CH3}$=7.4 Hz, 6H, -CH(CH$_3$)CH$_2$CH$_3$ of **10d$_1$** and **10d$_2$**). IR (CH_2Cl_2): υ 3700-3100 (H-bonded OH), 3600 (free OH), 3080-2790 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 220 (2,M$^+$), 202 (1,-H$_2$O), 163 (4,-*s*-Bu), 155 (78,-C$_5$H$_5$), 145 (6,-*s*-Bu,-H$_2$O), 137 (43,-C$_5$H$_6$,-OH), 97 (100,-C$_5$H$_6$,-*s*-Bu), 66 (92,C$_5$H$_6^+$), 57 (27,*s*-Bu$^+$). EI/HRMS *m/e*: 220.1465 (calc. for $C_{14}H_{20}O_2$ (M$^+$): 220.1463).

exo-5-*tert-Butyl*-endo-4,5-*epoxy*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-exo-3-*ol* **10e**

Following general procedure A [tetrahydrofuran (10 ml), 1.7 M *t*-BuLi in hexane (1.30 ml, 2.2 mmol), 1 h], **8** (176 mg, 1.1 mmol), gave, after work-up, a crude mixture in 88% yield. After flash chromatography (chloroform:benzene:ethyl acetate = 4:1:1) and crystallization an analytical sample of **10e** (99 mg, 41%) was obtained. No **9e** was isolated.

10e: white needles (petroleum-ether 40-60). m.p.: 101-102 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.17 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H$_8$ or H$_9$), 6.12 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H$_8$ or H$_9$), 3.84 (bs, 1H, H$_3$), 3.24 (d, $J_{2,4}$=0.7 Hz (W-coupling), 1H, H$_4$), 2.81 (bs, 1H, H$_1$ or H$_7$), 2.73 (bs, 1H, H$_1$ or H$_7$), 2.33 A of AB (dd, $J_{2,6}$=9.3 Hz, $J_{6,7}$=1.0 Hz, 1H, H$_6$), 2.25 B of AB (bd, $J_{1,2}$≈1.0 Hz, 1H, H$_2$), 1.99 A of AB (d, $J_{10a,10s}$=8.5 Hz, 1H, H$_{10s}$), 1.64 (bs, 1H, OH), 1.26 B of AB (dt, $J_{2,10s}$≈$J_{6,10s}$≈1.5 Hz, 1H, H$_{10s}$), 1.01 (s, 9H, -C(CH$_3$)$_3$). ^{1}H-NMR (400 MHz, $CDCl_3$, D_2O): *vide supra*, except δ 3.84 (d, $J_{2,3}$=2.9 Hz, 1H, H$_3$). IR (CH_2Cl_2): υ 3700-3090 (H-bonded OH), 3600 (free OH), 3050-2830 (C-H, unsat. and sat.) cm^{-1}. CI/MS: *m/e* (%) 220 (5,M$^+$), 203 (51,-OH), 163 (7,-*t*-Bu), 155 (76,-C$_5$H$_5$), 137 (100,-C$_5$H$_6$,-OH), 109 (66,-C$_5$H$_6$, -OH,-CO), 97 (50,-C$_5$H$_6$,-*t*-Bu), 66 (51,C$_5$H$_6^+$), 57 (40,*t*-Bu$^+$). Found: C 75.89, H 9.08 (calc. for $C_{14}H_{20}O_2$: C 76.33, H 9.15).

exo-4,5-*Epoxy*-exo-3-*phenyl*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-endo-3-*ol* **9f** *and* endo-4,5-*epoxy*-exo-5-*phenyl*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-exo-3-*ol* **10f**

Following general procedure A [tetrahydrofuran (10 ml), 2.0 M PhLi in hexane (1.00 ml, 2.0 mmol), 1 h], **8** (160 mg, 1.0 mmol), gave, after work-up, a crude mixture consisting of 74% **9f** and 26% **10f** (cap. GC). After flash chromatography (Al_2O_3, chloroform:benzene = 4:1) and crystallization, analytical samples of **9f** (83 mg, 35%) and **10f** (55 mg, 23%) were obtained.

9f: white plates (diisopropyl ether). m.p.: 124-125 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H, H$_{ortho}$), 7.39-7.34 (m, 2H, H$_{meta}$), 7.30-7.26 (m, 1H, H$_{para}$), 6.26 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H$_8$ or H$_9$), 6.11 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H$_8$ or H$_9$), 3.64 A of AB (dd, $J_{4,5}$=2.2 Hz, $J_{4,6}$=0.9 Hz (W-coupling), 1H, H$_4$), 3.44 B of AB (d, 1H, H$_5$), 3.05 (bs, 1H, H$_1$ or H$_7$), 2.90 (bs, 1H, H$_1$ or H$_7$), 2.43 A of AB (dd, $J_{2,6}$=7.0 Hz, 1H, H$_6$), 2.34 B of AB (d, 1H, H$_2$), 1.94 (s, 1H, OH), 1.89 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H$_{10s}$), 1.51 B of AB (dt, $J_{2,10a}$=$J_{6,10a}$=1.7 Hz, 1H, H$_{10a}$). IR (CH_2Cl_2): υ 3700-3120 (H-bonded OH), 3580 (free OH), 3110-2800 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 240 (6,M$^+$), 222 (5,-H$_2$O), 174 (55,-C$_5$H$_6$), 157 (38,-C$_5$H$_6$,-OH), 105 (90,C$_6$H$_5$C≡O$^+$), 77 (42,C$_6$H$_5^+$), 66 (100,C$_5$H$_6^+$). EI/HRMS *m/e*: 240.1153 (calc. for $C_{16}H_{16}O_2$ (M$^+$): 240.1150).

10f: white plates (diisopropyl ether). m.p.: 123-124 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H, H$_{ortho}$), 7.41-7.38 (m, 2H, H$_{meta}$), 7.34-7.31 (m, 1H, H$_{para}$), 6.10 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H$_8$ or H$_9$), 6.00 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H$_8$ or H$_9$), 4.04 (d, $J_{3,4}$=2.0 Hz, 1H, H$_3$), 3.62 (d, 1H, H$_4$), 3.06 (s, 1H, OH), 2.82 (bs, 1H, H$_1$ or H$_7$), 2.51 A of AB (d, $J_{2,6}$=6.5 Hz, 1H, H$_2$ or H$_6$), 2.06 B of AB (d, 1H, H$_2$ or H$_6$), 1.85 (bs, 1H, H$_1$ or H$_7$), 1.45 A of AB (d, $J_{10a,10s}$=9.0 Hz, 1H, H$_{10s}$), 1.04 B of AB (dt, $J_{2,10a}$≈$J_{6,10a}$≈1.6 Hz, 1H, H$_{10a}$). IR ($CHCl_3$): υ 3610-3100 (H-bonded OH), 3550 (free OH), 3100-2880 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 240 (6,M$^+$), 223 (4,-OH), 174 (9,-C$_5$H$_6$), 157 (27,-C$_5$H$_6$,-OH), 146 (11,-C$_6$H$_5$,-OH), 105 (100,C$_6$H$_5$C≡O$^+$), 77 (70,C$_6$H$_5^+$), 66 (63,C$_5$H$_6^+$). Found: C 79.94, H 6.68 (calc. for $C_{16}H_{16}O_2$: C 79.97, H 6.71).

exo-3-*Methyl*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-endo,exo-3,5-*diol* **20b**

Following general procedure B [tetrahydrofuran (10 ml), sat. $LiAlH_4$ in tetrahydrofuran (10 ml), 1 day], **6b** (49 mg, 0.28 mmol), gave, after work-up, a crude mixture consisting of 41% **6b**, 5% **7b** and 54% **20b** (cap. GC). Epoxy-alcohols **6b** and **7b** were removed by flash chromatography (*n*-hexane:ethyl acetate = 3:1) and subsequent elution with methanol gave 18 mg (36%) **20b** as a colorless oil.

Following general procedure B [tetrahydrofuran (10 ml), sat. $LiAlH_4$ in tetrahydrofuran (10 ml), 1 h], **7b** (51 mg, 0.29 mmol), gave, after work-up, 51 mg (97%) **20b** as a colorless oil.

20b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H$_8$ or H$_9$), 6.08 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H$_8$ or H$_9$), 3.77 (dd, $J_{4n,5}$=6.3 Hz, $J_{4x,5}$=2.4 Hz, 1H, H$_5$), 2.97, 2.93 and 2.69 (3 bs, 1H, 1H and 2H, H$_1$, H$_2$, H$_6$ and H$_7$), 1.92 A of AB (dd, $J_{4n,4x}$=13.8 Hz, 1H, H$_{4n}$), 1.69 (bs, 2H, OH), 1.64 B of AB (dd, 1H, H$_{4x}$), 1.46 A of AB (dt, $J_{10a,10s}$=8.0 Hz, $J_{1,10a}$≈$J_{7,10a}$ resp. $J_{1,10s}$≈$J_{7,10s}$≈1.8 Hz, 1H, H$_{10a}$ or H$_{10s}$), 1.46 (s, 3H, -CH$_3$), 1.33 B of AB (d, 1H, H$_{10a}$ or H$_{10s}$).

exo-4-*Deutero*-exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo,exo-3,5-*diol*, exo-4-*D*-**20b**
Following general procedure B [tetrahydrofuran (10 ml), $LiAlD_4$ in tetrahydrofuran (0.33 g/35 ml, 10 ml), 1 day], **6b** (99 mg, 0.56 mmol), gave, after work-up, a crude mixture containing 58% *exo*-4-D-**20b** (cap. GC). Epoxy-alcohols **6b** and **7b** were removed by flash chromatography (*n*-hexane:ethyl acetate = 3:1) and subsequent elution with methanol gave 48 mg (48%) *exo*-4-D-**20b** as a colorless oil.
Following general procedure B [tetrahydrofuran (10 ml), $LiAlD_4$ in tetrahydrofuran (0.33 g/35 ml, 10 ml), 1 h], **7b** (75 mg, 0.42 mmol), gave, after work-up, 76 mg (quant.) *exo*-4-D-**20b** as a colorless oil.
exo-4-D-**20b**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.08 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 3.76 (d, $J_{4n,5}$=6.3 Hz, 1H, H_5), 2.97, 2.92 and 2.69 (3 bs, 1H, 1H and 2H, H_1, H_2, H_6 and H_7), 1.89 (d, 1H, H_{4n}), 1.63 (bs, 2H, OH), 1.46 A of AB (bd, $J_{10a,10s}$=8.0 Hz, 1H, H_{10a} or H_{10s}), 1.46 (s, 3H, -CH_3), 1.33 B of AB (d, 1H, H_{10a} or H_{10s}). EI/HRMS *m/e*: 181.1213 (calc. for $C_{11}H_{15}O_2D$ (M^+): 181.1213).

endo-4-*Deutero*-exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo,exo-3,5-*diol*, endo-4-*D*-**20b**
Following general procedure B [tetrahydrofuran (20 ml), $LiAlH_4$ in tetrahydrofuran (0.20 g/20 ml, 15 ml), 2.5 h], **24** (150 mg, 0.84 mmol, *vide infra*), gave, after work-up, 148 mg (98%) *endo*-4-D-**20b** as a colorless oil, which slowly solidified.
endo-4-D-**20b**: white powder (*n*-hexane/dichloromethane). m.p.: 107-109 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.08 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 3.77 (bs, 1H, H_5), 2.97, 2.92 and 2.69 (3 bs, 1H, 1H and 2H, H_1, H_2, H_6 and H_7), 1.62 (bs, 1H, H_{4x}), 1.46 A van AB (dt, $J_{10a,10s}$=8.0 Hz, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10a}\approx J_{7,10s}\approx$1.8 Hz, 1H, H_{10a} or H_{10s}), 1.46 (s, 3H, -CH_3), 1.33 B of AB (d, 1H, H_{10a} or H_{10s}), 1.32 (bs, 2H, OH). IR ($CHCl_3$): υ 3660-3090 (H-bonded OH), 3600 (free OH), 3060 (C-H, unsat.), 3030-2800 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 181 (0.2,M^+), 166 (48,-CH_3), 114 (18,-C_5H_6,-H), 99 (6,-C_5H_6,-CH_3), 98 (43,-C_5H_6,-OH), 97 (14,-C_5H_6,-H_2O), 81 (5,-C_5H_6,-OH,-OH), 80 (5,-C_5H_6,-OH,-H_2O), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 166.0979 (calc. for $C_{10}H_{12}O_2D$ (M^+-CH_3): 166.0978).

4-*Deutero*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-3-*one* **22**
This compound was synthesized according to the procedure described by Miura *et al.*[10], using a solution of sodium (42 mg, 1.8 mmol) and *endo*-**1** (1.0 g, 6.8 mmol) in CH_3OD (10 ml). After work-up, 0.94 g (94%) **22** was isolated as a white solid. An analytical sample was obtained by crystallization.
22: white powder (*n*-pentane). m.p.: 62-64°C. ^{1}H-NMR (100 MHz, $CDCl_3$): δ 7.41 (d, $J_{5,6}$=2.5 Hz, 1H, H_5), 5.90 A of AB (dd, $J_{8,9}$=5.4 Hz, $J_{1,9}$=2.9 Hz, 1H, H_9), 5.77 B of AB (dd, $J_{7,8}$=2.9 Hz, 1H, H_8), 3.50-3.38 (m, 1H, H_6), 3.18 (bs, 1H, H_1), 3.01-2.96 (m, 1H, H_7), 2.78 (dt, $J_{1,2}\approx J_{2,6}\approx$5.0 Hz, 1H, H_2), 1.75 A of AB (dt, $J_{10a,10s}$=8.4 Hz, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10s}\approx J_{7,10s}\approx$1.7 Hz, 1H, H_{10a} or H_{10s}), 1.62 B of AB (d, 1H, H_{10a} or H_{10s}). IR ($CHCl_3$): υ 3050 (C-H, unsat.), 3030-2800 (C-H, sat.), 1690 (C=O, conj.), 1555 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 147 (10,M^+), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 147.0794 (calc. for $C_{10}H_9OD$ (M^+): 147.0795).

endo-4-*Deutero*-exo-4,5-*epoxy*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **23**
20% Aqueous Na_2CO_3 (7 ml) and 35% H_2O_2 (10 ml) were added to a solution of **22** (524 mg, 3.6 mmol) in acetone (10 ml) at 0 °C and the resulting mixture was stirred for 20 minutes under a nitrogen atmosphere. The crude mixture was diluted with water (10 ml) and extracted with dichloromethane (3x). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give 578 mg (97%) **23** as a white solid.
23: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.08 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$=2.5 Hz, 1H, H_9), 6.03 B of AB (dd, $J_{7,8}$=2.8 Hz, 1H, H_8), 3.60 (d, $J_{5,6}$=1.6 Hz, 1H, H_5), 3.24 (bs, 1H, H_7), 3.11 (bs, 1H, H_1), 3.10 (t, $J_{1,2}$=4.1 Hz, 1H, H_2), 2.77 (ddd, $J_{2,6}$=6.5 Hz, $J_{6,7}$=4.6 Hz, 1H, H_6), 1.62 A of AB (dt, $J_{10a,10s}$=8.6 Hz, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10s}\approx J_{7,10s}\approx$1.5 Hz, 1H, H_{10a} or H_{10s}), 1.46 B of AB (d, 1H, H_{10a} or H_{10s}). EI/MS: *m/e* (%) 163 (2,M^+), 98 (34,-C_5H_5), 66 (100,$C_5H_6^+$).

exo-4-*Deutero*-endo-4,5-*epoxy*-exo-5-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-exo-3-*ol* **24** *and* endo-4-*Deutero*-exo-4,5-*epoxy*-exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-endo-3-*ol* **29**
Following general procedure A [tetrahydrofuran (20 ml), 1.3 M MeMgI in ether (2.40 ml, 3.1 mmol), 3 days], **23** (400 mg, 2.5 mmol), gave, after work-up, a crude mixture consisting of 81% **24** and 19% **29** (cap. GC) in quantitative yield. After flash chromatography (*n*-hexane:ethyl acetate = 3:1), 312 mg (70%) **24** and 50 mg (11%) **29** were both obtained as a white solid. Analytical samples were obtained by crystallization.
24: white needles (*n*-hexane). m.p.: 101-102 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{7,8}$=3.0 Hz, 1H, H_8), 5.88 B of AB (dd, $J_{1,9}$=3.0 Hz, 1H, H_9), 3.78 (bs, 1H, H_3), 2.99 A of AB (dt, $J_{2,6}$=10.5 Hz, $J_{1,2}\approx J_{2,3}\approx$3.7 Hz, 1H, H_2), 2.93 (bs, 1H, H_7), 2.89 (bs, 1H, H_1), 2.79 B of AB (dd,

$J_{6,7}$=3.6 Hz, 1H, H_6), 1.67 (bd, $J_{3,OH}$≈3.8 Hz, 1H, OH), 1.49 A van AB (dt, $J_{10a,10s}$=8.1 Hz, $J_{1,10a}$≈$J_{7,10a}$ resp. $J_{1,10s}$≈$J_{7,10s}$≈1.8 Hz, 1H, H_{10a} or H_{10s}), 1.43 (s, 3H, -CH_3), 1.34 B of AB (bd, 1H, H_{10a} or H_{10s}). IR ($CHCl_3$): υ 3680-3090 (H-bonded OH), 3610 (free OH), 3060 (C-H, unsat.), 3030-2810 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 179 (2,M^+), 161 (5,-H_2O), 113 (32,-C_5H_6), 98 (28,-C_5H_6,-CH_3), 96 (30,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 179.1057 (calc. for $C_{11}H_{13}O_2D$ (M^+): 179.1057).

29: white needles (*n*-hexane). m.p.: 105-106 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 6.16 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 3.16 (s, 1H, H_5), 2.98 (bs, 1H, H_1 or H_7), 2.96-2.94 (m, 1H, H_1 or H_7), 2.89 A of AB (dd, $J_{2,6}$=7.8 Hz, $J_{6,7}$=4.4 Hz, 1H, H_6), 2.52 B of AB (dd, $J_{1,2}$=4.1 Hz, 1H, H_2), 1.58 (bs, 1H, OH), 1.49 A of AB (dt, $J_{10a,10s}$=8.2 Hz, $J_{1,10a}$≈$J_{7,10a}$ resp. $J_{1,10s}$≈$J_{7,10s}$≈1.8 Hz, 1H, H_{10a} or H_{10s}), 1.40 (s, 3H, -CH_3), 1.32 B of AB (bd, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3660-3040 (H-bonded OH), 3600 (free OH), 3040-2820 (C-H, unsat. and sat.) cm^{-1}. EI/MS: *m/e* (%) 179 (2,M^+), 113 (13,-C_5H_6), 98 (11,-C_5H_6,-CH_3), 96 (11,-C_5H_6,-OH), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 179.1055 (calc. for $C_{11}H_{13}O_2D$ (M^+): 179.1057).

endo-4,5-*Epoxy*-exo-5-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **25b**

To a suspension of PCC (362 mg, 1.7 mmol) in dry dichloromethane (20 ml) a solution of **7b** (200 mg, 1.1 mmol) was added and the mixture stirred at room temperature. The reaction was monitored by TLC and after standard work-up[15] 150 mg (77%) **25b** (purity > 92%, cap. GC) was isolated as a colorless oil. An analytical sample was obtained by flash chromatography (*n*-hexane:ethyl acetate = 3:1)[16].

25b: ^{1}H-NMR (100 MHz, $CDCl_3$): δ 6.12 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 5.98 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.6 Hz, 1H, H_8 or H_9), 3.14-2.80 (m, 5H, H_1, H_2, H_4, H_6 and H_7), 1.58 A of AB (bd, $J_{10a,10s}$=8.3 Hz, 1H, H_{10a} or H_{10s}), 1.54 (s, 3H, -CH_3), 1.41 B of AB (bd, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3010-2820 (C-H, unsat. and sat.), 1730 (C=O) cm^{-1}. CI/MS: *m/e* (%) 177 (5,M^++1), 159 (7,-H_2O), 111 (100,-C_5H_6), 82 (47,$C_5H_6O^+$), 66 (66,$C_5H_6^+$). EI/HRMS *m/e*: 176.0840 (calc. for $C_{11}H_{12}O_2$ (M^+): 176.0837).

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2. The regio- and stereoselectivity of the addition of (a) organometallics and (b) halogens to *endo*- and *exo*-tricyclodecadienones **1** were described in two previous papers (accepted for publication in *Tetrahedron*).
3. For a preliminary publication, see: Lange, J.H.M.; Sommerdijk, N.A.J.M.; Dols, P.P.M.A.; Arnouts, E.G.; Klunder, A.J.H.; Zwanenburg, B. *Tetrahedron Lett.*, **1991**, *32*, 3127.
4. The results shown in tables 1 and 2 were obtained by adhering strictly to the reaction conditions mentioned in the experimental section, as product ratios proved sensitive to small changes in the experimental procedure.
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9. Preliminary experiments showed that hardly any inverted epoxy alcohol **7** was obtained from the addition of more bulky Grignard reagents such as *n*-butyl, *sec*-butyl and *tert*-butyl magnesium halides. Apart from formation of some non-inverted epoxy alcohols **6**, considerable reduction of **5** to alcohol **6a** was observed. Apparently, carbonyl addition of these relatively bulky Grignard reagents is considerably retarded, most likely due to unfavorable steric interaction with the *exo* epoxide function in **5**. As these Grignard reagents possess β-hydrogens, reduction of the carbonyl function is now

feasible and apparently more favorable. A similar result was found earlier in our attempts to deprotonate **5** with lithium diisopropyl amide in tetrahydrofuran[3]. Here too, exclusive formation of **6a** was observed by efficient β-hydrogen transfer from the lithium amide to the carbonyl function. The absence of any reduction product in the addition of organolithium reagents (Table 1) is most likely due to higher reactivity of these organometallics toward nucleophilic additions as compared with Grignard reagents. (Klunder, A.J.H.; Schuurman, R.F.W.; Zwanenburg, B. to be published)

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11. After addition of $LiAlD_4$, a fast conversion of **6b** to *exo*-4-D-**20b** was observed. After one day, however, the rate of reaction had decreased considerably. Rather than wait until complete conversion was achieved, the reaction mixture was quenched after one day (approximately 50% conversion). The drop in the rate of reaction can be explained by assuming a sharp drop in the rate of the Payne rearrangement of **6b** to **7b**, which was also observed in the addition of methyllithium to **5**. Based on this assumption, at this stage, the rate of the direct reduction can become comparable to or higher than that of the Payne rearrangement and direct reduction will predominate over the indirect pathway. As a result, Liu and coworkers[12] observed a mixture of *endo*- and *exo*-4-D-**20b** after prolonged reaction times (6-8 days), the ratio of both products depending on the point at which the Payne rearrangement is slower than the direct reduction.
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16. The crude product is sufficiently pure for further synthetic purposes. Purification of **25b** by flash chromatography is therefore not necessary and has to be avoided as it was accompanied by an almost 50% loss of material.

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