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Regio- and Stereoselectivity of Additions of Organometallics to endo- and exo-Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-ones

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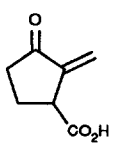
Abstract: *The regio- and stereoselectivity of the addition of selected organometallics to* endo- *and* exo-*tricyclodecadienones* **12**, **18** *and* **21** *are described. RLi and* R_2CuLi *add with complete 1,2- and 1,4-regioselectivity, respectively, the additions of RMgX and RMgX/CuX are only slightly less selective. Additions to* **12** *and* **21** *occur from the* convex exo-*face only, irrespective of the nature of both reagent and substrate. In contrast, organometallic species add from both the* concave *and the* convex *face to tricyclic ester* **18**, *with a selectivity that depends on the type of organometallic reagent. The observed stereoselectivities of the additions are rationalized by invoking steric control by the* C_8-C_9 *ethylene bridge in* **12**, *by the* C_{10} *methylene bridge in* **21** *and by both the* C_8-C_9 *ethylene bridge and the* exo-*ester function at* C_2 *in tricyclic ester* **18**.

INTRODUCTION

Natural products containing the cyclopentanone or cyclopentenone substructure generally show significant biological activity. The pharmacological importance of cyclopentanoids was particularly recognized in the early 1960s when prostaglandins were isolated and established to be essential human fatty acid hormones that control a multitude of important physiological processes[1]. Later, other biologically



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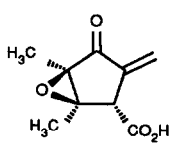

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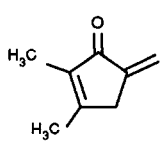

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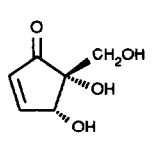

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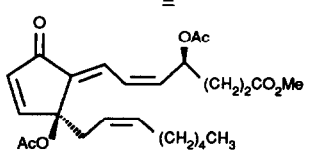

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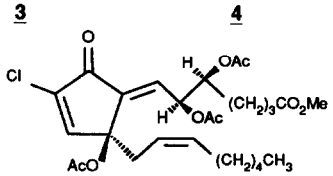

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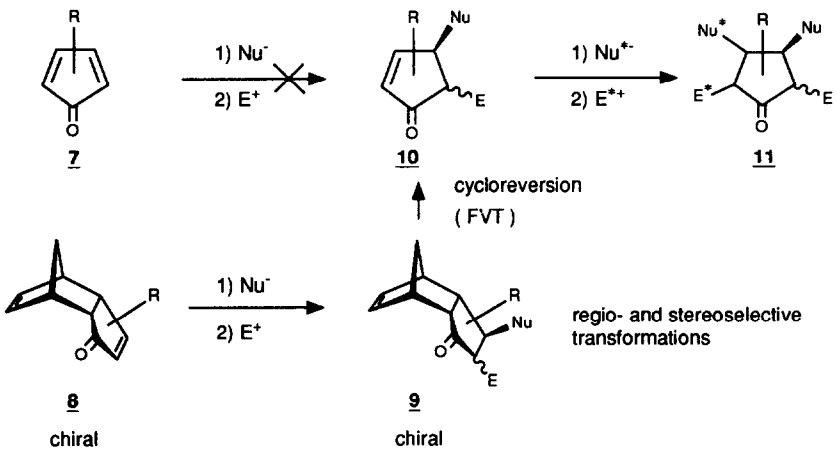
interesting cyclopentanoids were discovered which possess antibiotic and/or antitumor activity[2]. Examples are sarkomycin **1**, methylenomycins A **2** and B **3**, pentenomycin **4**, and a series of marine eicosanoids related to prostaglandins, such as clavulone **5** and punaglandin **6**. These discoveries initiated enormous synthetic activity aimed at developing effective stereo- and enantioselective methods for the construction of such highly functionalized cyclopentanoids[3-5].

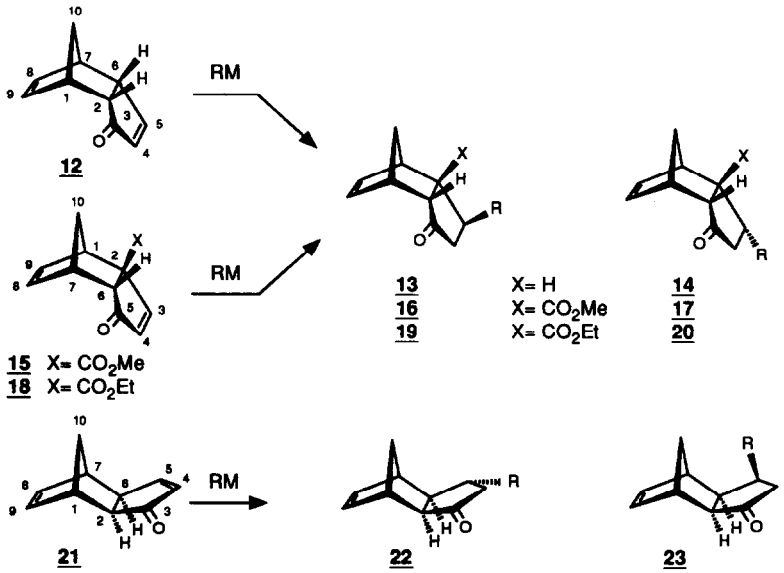
A most direct route would involve the chemical transformation of appropriately substituted cyclopentadienones **7**, *e.g.* by conjugate addition of suitable nucleophiles followed by electrophilic trapping of the enolate (Scheme 1; upper line). This approach, however, is not feasible as cyclopentadienones **7** are

Scheme 1



highly reactive molecules[6] that generally dimerize at temperatures above -100 °C. Therefore, we explored the *endo*-tricyclo[5.2.1.$0^{2,6}$]decadienone system **8** as a synthetic equivalent of cyclopentadienone. Being in essence the Diels-Alder adduct of a cyclopentadienone and cyclopentadiene, this tricyclic cyclopentenone **8** actually constitutes a cyclopentadienone **7** in which one of the double bonds is masked. Chemical transformation of the remaining enone system, *e.g.* by conjugate addition to give **9**, followed by a retro-Diels-Alder reaction, using the technique of flash vacuum thermolysis (FVT), regenerates this masked enone functionality to yield functionalized cyclopentenones **10** or eventually cyclopentanones **11** (Scheme 1). This synthetic strategy has successfully been applied by us[4] and others[5] for the synthesis of a large variety of naturally occurring cyclopentanoids or pharmacologically important structures. The success of this approach is primarily attributable to two factors, *viz.* (i) the ready availability of both optical antipodes of parent *endo*-tricyclodecadienone **12** by enzymatic resolution of one of its precursors[5b,7,8], and (ii) the high regio- and stereoselectivity observed for the 1,4- or 1,2-addition of nucleophiles to the enone moiety. Due to shielding of the *concave endo*-face in **12** by the norbornene C_8-C_9 bridge, attack of the reagent on the enone moiety at this side of the molecule is severely hindered and addition preferentially occurs at the sterically less hindered *convex exo*-face. Hence, starting from enantiopure *endo*-tricyclodecadienone **12** nucleophilic 1,4-addition followed by protonation generally leads to a single, enantiopure addition product **13** (Scheme 2). Subsequent cycloreversion then leads to an enantiopure cyclopentenone with well-defined stereochemistry. So far no

Scheme 2



nucleophilic 1,4-additions to **12** have been reported involving the occurrence of *endo*-addition product **14**.

Preliminary studies concerning nucleophilic 1,4-additions to the sterically more demanding tricyclic ester **18** showed that, when employing relatively small nucleophiles, such as the cyanide anion and MeMgI in the presence of CuI, the *exo*-ester function does not interfere much with the incoming nucleophile and thus gives predominantly the *exo-convex*-addition product **19**[4c]. However, Marchand *et al.* reported that addition of dimethyllithiumcuprate to **15** and 7-methyl-**15** proceeded with the formation of a considerable amount of the *endo-concave* 1,4-addition products **17a**[9] and 7-methyl-**17a**[10], respectively. These unexpected results indicated that the stereochemistry of these nucleophilic 1,4-additions may be strongly dependent on the nature of both the reagent and the substrate.

In contrast to its *endo*-isomer **12**, so far only nucleophilic 1,4-additions to some 4-substituted *exo*-tricyclodecadienones **21** (4-SC_6H_5 and 4-$(CH_2)_4CH_3$) have been reported[11]. Sole formation of the *convex* addition products **22** was observed for the addition of nucleophiles to these derivatives of **21**. No mention was made of the formation of their epimers **23**.

In order to establish the stereochemical influence of steric and configurational features of the tricyclic substrate as well as the effect of the nature of the organometallic reagent on nucleophilic additions to both the *endo*- and *exo*-tricyclodecadienone system, we undertook a comparative study of the 1,4- and 1,2-additions of some representative organometallic nucleophiles to *endo*-tricyclodecadienone **12**, *endo*-tricyclic ester **18** and *exo*-tricyclodecadienone **21**.

1,4-ADDITION OF ORGANOMETALLIC REAGENTS

Results

The conjugate addition to tricyclodecadienones **12**, **18** and **21** was studied for four selected organometallic reagents, *viz.* MeMgI in the presence of CuCl, Me_2CuLi, *n*-Bu_2CuLi and Ph_2CuLi[12] under standard experimental conditions (*cf.* experimental section). In all cases the reactions proceeded smoothly and the addition products were obtained in excellent yields (Table 1).

Table 1. Regio- and Stereoselectivity of 1,4-Additions of Organometallics to **12**, **18** and **21**.

entry	substrate	alkylating agent	yield [a]	product composition	
				1,2-adduct	1,4-adduct
1	**12**	MeMgI/CuCl	77%	3% **30a**	97% **13a**
2	**12**	Me_2CuLi	84%	----	100% **13a**
3	**12**	*n*-Bu_2CuLi	quant.	----	100% **13b**
4	**12**	Phe_2CuLi	93%	----	100% **13c**
5	**18**	MeMgI/CuCl	80%	----	80% **19a**, 20% **20a**
6	**18**	Me_2CuLi	60%	----	75% **19a**, 25% **20a**
7	**18**	*n*-Bu_2CuLi	75%	----	88% **19b**, 12% **20b**
8	**18**	Phe_2CuLi	92%	----	33% **19c**, 67% **20c**
9	**21**	MeMgI/CuCl	84%[b]	4% **32a**	96% **22a**
10	**21**	Me_2CuLi	82%[b]	----	100% **22a**
11	**21**	*n*-Bu_2CuLi	83%	----	100% **22b**
12	**21**	Phe_2CuLi	79%	----	100% **22c**

[a] after purification [b] crude product.

The addition of dimethyl-, di-*n*-butyl- and diphenylcopperlithio compounds to all three tricyclodecadienones **12**, **18** and **21** appeared to be completely 1,4-regioselective (Table 1, entries 2-4, 6-8 and 10-12). No 1,2-addition products were formed at all. Exclusive 1,4-addition was also observed when methylmagnesium iodide in the presence of copper(I) chloride was added to **18** (entry 5). However, for **12** and **21** a small amount, 3-4%, of a 1,2-addition product was formed as well (entries 1 and 9).

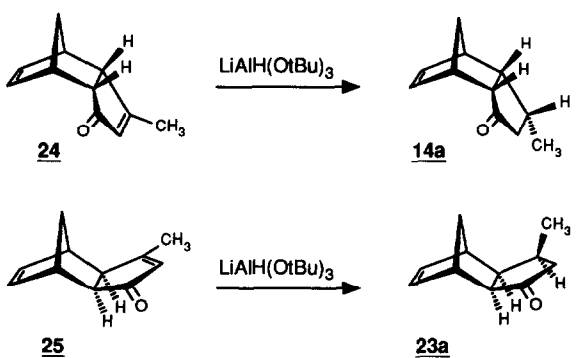
The conjugate nucleophilic additions to parent *endo*- and *exo*-tricyclodecadienones **12** and **21** appeared to be completely stereoselective. Reaction of **12** and **21** with either organometallic reagent gave only a single 1,4-addition product to which, on basis of detailed ^{1}H-NMR studies (*vide infra*), configurations **13** and **22**, respectively, were assigned. Scrutinizing the reaction mixture did not reveal any trace of their epimers **14** and

23. Conjugate addition to tricyclic ester **18** appeared to be much less stereoselective. With MeMgI/CuCl, Me_2CuLi and *n*-Bu_2CuLi a considerable amount (12-25%) of **20** accompanied the formation of **19**. Most unexpectedly, addition of diphenyllithium cuprate, which occurs in an excellent total yield of 92%, was found to give **20c** as the main product (Table 1, entry 8, ratio of **19c** to **20c** is 1:2).

Structural assignments

The gross structures of the products obtained were all deduced from their mass, IR and NMR data, while the relative amounts were determined quantitatively by capillary gas chromatography and ^{1}H-NMR spectroscopy. However, the unequivocal assignment of the configuration (*endo* or *exo*) of the newly introduced substituent at C_5 in the 1,4-addition products of **12** and **21**, or at C_3 in the 1,4-addition products of **18** required a more detailed ^{1}H-NMR analysis of all conceivable 1,4-addition products. For this purpose, we selected methyl substituted tricyclodecenones, *viz.* **13a**, **14a**, **19a**, **20a**, **22a** and **23a**. Whereas **13a**, **19a**, **20a** and **22a** were obtained directly from the 1,4-additions with either Me_2CuLi or MeMgI/CuCl, *endo*-5-methyl-*endo*- and *endo*-5-methyl-*exo*-tricyclodecenones **14a** and **23a** were obtained by reduction of 5-methyl-*endo*- and 5-methyl-*exo*-tricyclodecadienones **24** and **25**[16], respectively, with $LiAlH(OtBu)_3$[17] (Scheme 3). Similar to the addition of organometallic reagents to **12** and **21**, 1,4-hydride addition to **24** and **25**

Scheme 3



also turned out to be completely stereoselective producing *endo*-5-methyl substituted tricyclodecenones **14a** and **23a** as single 1,4-addition products. These tricyclodecenones were distinctly different from **13a** and **22a** obtained by conjugate methyl addition to **12** and **21**, respectively. After having assigned all resonances in the ^{1}H-NMR spectra of all methyl substituted tricyclodecenones using decoupling techniques, it still proved necessary to use NOE experiments to reveal the configuration at the carbon atom bearing the methyl substituent. For this purpose, the methyl resonance was irradiated while the intensity of the other signals was monitored. Assuming that protons effected by this irradiation of the methyl group must be within 3 Å[18,19] of the nearest methyl proton, the configuration at the methyl bearing carbon atoms was established for all six tricyclodecenones. Table 2 shows that there is a good correlation between the expected and observed NOE effects in each case. Conclusive evidence comes especially from the observation of a relatively strong NOE effect for H_8 in **14a** and H_9 in **20a**, which can only be explained satisfactory if in both compounds the methyl group is in the *endo*-position. As a consequence, **13a** and **19a** must be the corresponding *exo*-substituted

Table 2. Observed NOE-Effects in **13a**, **14a**, **19a**, **20a**, **22a** and **23a**.

	distance between H_x and the nearest hydrogen of the methyl group (in Å) [a,18,19].					
H_x	**13a**	**14a**	**19a**	**20a**	**22a**	**23a**
H_1	>5	>5	3.3	2.9	>5	>5
H_2	4.1	3.0	----	----	4.1	5.0
H_3	----	----	2.4	2.6	----	----
H_{4n}	2.9	2.6	2.9	2.6	3.0	2.5
H_{4x}	2.5	3.0	2.5	3.0	2.5	3.0
H_5	2.5	2.5	----	----	2.5	2.5
H_6	2.5	4.9	4.4	5.0	2.5	3.0
H_7	3.2	2.9	>5	>5	3.1	2.4
H_8	4.3	2.5	>5	4.5	4.8	4.7
H_9	>5	4.5	4.2	2.4	>5	>5
H_{10a}	>5	5.0	>5	4.9	4.5	2.7
H_{10s}	5.0	4.9	>5	5.0	>5	3.9

[a] A NOE-effect is expected for protons within 3 Å of the nearest proton of the methyl group. If a NOE-effect is indeed observed, the corresponding distance is underlined.

analogs. These assignments agree nicely with the NOE effects observed for H_{4n}[20] in **14a** and **20a**, for H_6 in **13a** and for H_{4x} in **13a** and **19a**. The observation of a NOE effect for H_6 and H_{4x} in **22a** and for H_{4n} in **23a** permits their characterization as the *exo*- and *endo*-5-methyl substituted *exo*-tricyclodecenones, respectively. By analogy of their ^{1}H-NMR spectra with those of the methyl substituted compounds, the *n*-butyl- and phenyl-addition products were assigned the structures **13b,c**, **19b,c**, **20b,c** and **22b,c**, respectively (*cf.* experimental section). Because of the deviating selectivity during the reaction of Phe_2CuLi with tricyclic ester **18** we tried to find additional evidence to substantiate the assignment of structures **19c** and **20c**. Figure 1 shows the AM1-minimized[21] structures for *exo*-5-phenyl **19c** and *endo*-5-phenyl **20c**. It is immediately clear that the orientation of the phenyl substituent with respect to the tricyclic framework is completely different in both compounds. In **19c** the $-OCH_2CH_3$ protons are in the shielding cone of the phenyl ring, whereas H_{4x}[20] is in the deshielding cone. In **20c** no significant effect of the phenyl group on the $-OCH_2CH_3$ and H_{4x} resonances is expected. Comparison of the chemical shift values of $-OCH_2CH_3$ and H_{4x} in **19a,b** and **20a,b** with those of **19c** and **20c**, shows an excellent agreement between predicted and observed (de)shielding effects, which unequivocally confirms the assignment of structures **19c** and **20c** (Table 3).

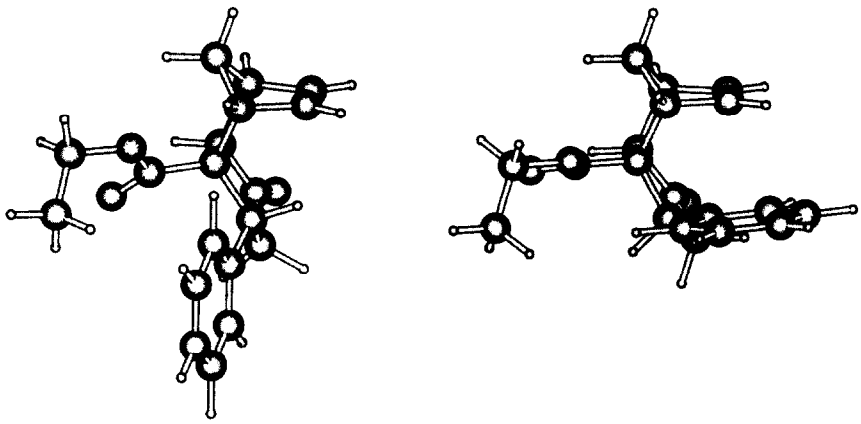


Figure 1. AM1-minimized structures of **19c** (*left*) and **20c** (*right*), in a view almost parallel to C_2-C_6 and C_8=C_9.

Table 3. Chemical Shift of Selected Protons in **19a-c** and **20a-c**.

		δ [a]			
compound	R	H_{4n}	H_{4x}	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$
19a	Me	2.25	2.31	4.24	1.32
19b	*n*-Bu	2.24	2.40	4.24	1.32
19c	Ph	2.47	3.05	3.67 / 3.58	0.86
20a	Me	1.84	2.32	4.24-4.16	1.29
20b	*n*-Bu	2.40-2.27		4.26-4.14	1.29
20c	Ph	2.68	2.59	4.35-4.28	1.34

[a] in ppm, relative to TMS as an internal standard.

Discussion

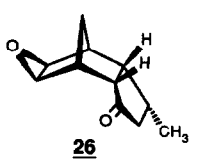
The factors affecting the stereochemistry of addition of organocuprates to (poly)cyclic enones are not completely understood[24]. Approach of the reagent is in general perpendicular to the plane of the enone and is sensitive to steric as well as stereoelectronic factors. Even substituents not directly attached to the reacting region may affect the stereochemistry and the amount of conjugate addition by their spatial proximity to the reactive site.

The observation of complete stereoselectivity for the conjugate addition of organometallics to the parent *endo*- and *exo*-tricyclodecadienone **12** and **21**, irrespective of the size and the nature of the

organometallic reagent manifestly shows the steric control exerted by the C_8-C_9 ethylene bridge in **12** and the C_{10} methylene bridge in **21**. For both tricyclodecadienones addition occurs exclusively at the *convex* face of the molecule and consequently leads to 5-*exo*-substituted tricyclodecenones. An *exo*-ester function at the *convex* face of the *endo*-tricyclodecadienone system obviously increases the steric bulk on this face of the molecule and, as a consequence, nucleophilic addition at this face may be less favorable. Indeed, a reduced stereoselectivity is observed upon addition of either organometallic reagent to **18**. The methyl- and *n*-butyl-substituted organometallics still show considerable preference for addition from the *convex* face, whereas the phenyl containing reagent favors attack from the *concave* face. As will be shown below these differences in selectivity are in agreement with the general assumption that the initial step in the reaction of organocuprates with α,β-unsaturated ketones is a single electron transfer (SET) from the organocopper(I) species to the ketone[24], resulting in the formation of an anionic enone radical and a cationic organocuprate radical $[R_4Cu_2Li_2]^{+\cdot}$. For R=alkyl (*e.g.* Me and *n*-Bu) this cationic organocuprate radical is less stable than for R=aryl (*e.g.* Ph), and product formation will be kinetically controlled. For the addition of Me_2CuLi and *n*-Bu_2CuLi to **18**, the balance between steric shielding of the *endo*-face by the norbornene C_8-C_9 double bond and shielding of the *exo*-face by the ester moiety is apparently in favor of *convex* addition. For R=aryl, in contrast, the intermediate cationic organocuprate radical is longer living, which is also demonstrated by the coupling of two phenyl radicals to give biphenyl as a by-product in the reaction of Phe_2CuLi with **12**, **18** and **21** (*cf.* experimental section). Under these conditions product formation will be more thermodynamically controlled, resulting in a preference for *concave* addition in the reaction of Phe_2CuLi with **18**. Stereoelectronic effects, such as a conceivable interaction of the norbornene C_8-C_9 double bond with the copper bonded phenyl group, can however not be excluded.

Spontaneous epoxidation of some 1,4-adducts by molecular oxygen

It is of interest to note that four of the substituted tricyclodecenones used in this study, *viz.* **14a**, **19a**, **20a** and **23a** are rather unstable on prolonged standing. After 1-2 months in the refrigerator at 4 °C in each case a new product was formed in considerable amounts. According to their ^{1}H-NMR spectra all new compounds still contained the basic tricyclodecane skeleton, but clearly lacked the C_8-C_9 double bond. Furthermore, in their ^{1}H-NMR spectra two new resonances, integrating for one proton each, had emerged around 3.3 ppm while one of the bridge protons (*i.e.* H_{10a} or H_{10s}) had shifted 0.6 ppm toward higher field. Conclusive information about the structures of the newly formed products was derived from the mass spectrum of the product arising from **19a** which could readily be isolated from the mixture. The molecular mass had increased with 16, suggesting the occurrence of epoxide **27**. Indeed, epoxidation of



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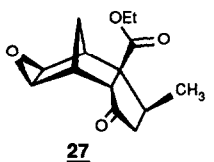

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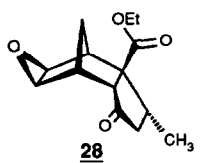

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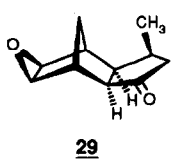

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tricyclodecenone **19a** with *meta*-chloroperbenzoic acid furnished tricyclic *exo*-8,9-epoxyketone **27**, whose spectral features were identical with those of the unknown product. On the basis of this structural assignment it must be concluded that on standing at room temperature, tricyclodecenones **14a**, **19a**, **20a** and **23a** slowly

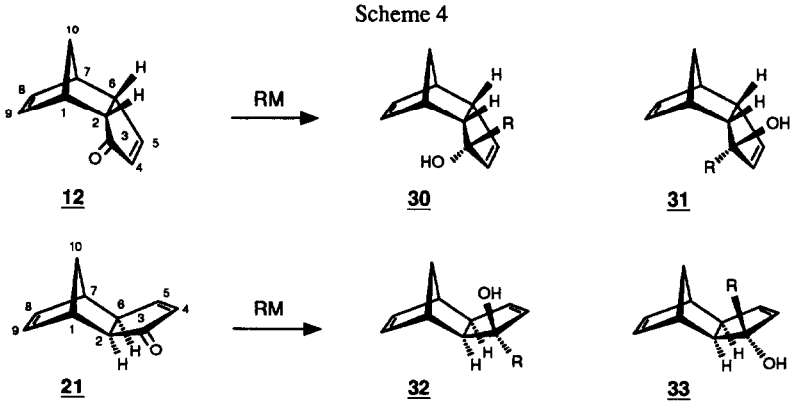
undergo epoxidation of the norbornene double bond to yield epoxides **26**-**29**. As no oxidizing agent other than air oxygen was present we assume this spontaneous epoxidation of the above tricyclodecenones is caused by their exposure to air. Although epoxidation of norbornene and dicyclopentadiene with molecular oxygen is known, it generally requires radical[25a], metal-catalyzed[25b-e] or photochemical[25f,g] initiation, often at elevated temperature. The spontaneous oxygenation of dicyclopentadiene, however, has been reported[25e,f,26]. Attempts to generate epoxide **27** by bubbling oxygen through a solution of **19a** in tetrachloromethane failed. Also in the presence of dibenzoylperoxide as a radical initiator no epoxidation was observed. Apparently, the epoxidation is a delicate process. Although no satisfactory explanation for this epoxidation of the norbornene double bond in these tricyclodecenones by molecular oxygen can be given yet, it is evident that the structural features of the tricyclodecenones play a crucial role, as, under identical conditions, no oxidation products are formed at all from the thermodynamically more stable and sterically less strained epimers **13a** and **22a**[27]. It seems that some steric strain in the tricyclodecenone is necessary to initiate the epoxidation process. This view is supported by a report of Bartlett and Banavali[28] on the spontaneous oxygenation of strained cyclic olefins. Work is currently in progress to shed light on the structural requirements as well as the conditions needed for this intriguing epoxidation of tricyclodecenones by molecular oxygen.

1,2-ADDITION OF ORGANOMETALLIC REAGENTS

Results

The regio- and stereoselectivity of 1,2-additions were investigated for parent *endo*- and *exo*-tricyclodecadienones **12** and **21** employing methylmagnesium iodide, methyllithium, *n*-butyllithium, *sec*-butyllithium and phenyllithium as reagents (Scheme 4 and Table 4). Yields are generally close to 90% according to gas

Scheme 4



a: R= Me **b**: R=n-Bu **c**: R= s-Bu **d**: R= Ph
RM= see Table 4

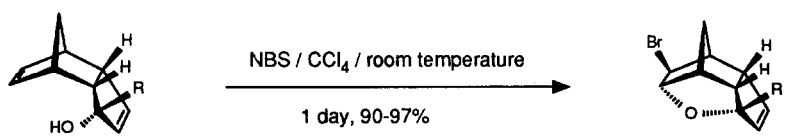
chromatographic and ^{1}H-NMR data. During isolation by column chromatography on silica, however, loss of some alcoholic product had to be accepted. Except reactions of **12** and **21** with MeMgI, which also gave some of the corresponding 1,4-adducts, all additions studied were completely regio- and stereoselective. This is also true for *sec*-butyllithium although it gave a mixture of two diastereomers in a ratio of nearly 1:1 (according to 400 MHz ^{1}H-NMR). However, this mixture is not the result of competitive addition from the

Table 4. Regio- and Stereoselectivity of 1,2-Additions of Organometallics to **12** and **21**.

entry	substrate	alkylating agent	yield [a]	product composition	
				1,2-adduct	1,4-adduct
1	**12**	MeMgI	76%	93% **30a**	7% **13a**
2	**12**	MeLi	53%	100% **30a**	----
3	**12**	*n*-BuLi	78%	100% **30b**	----
4	**12**	*sec*-BuLi	73%	100% **30c** [b]	----
5	**12**	PheLi	73%	100% **30d**	----
6	**21**	MeMgI	88%[c]	66% **32a**	34% **22a**
7	**21**	MeLi	71%	100% **32a**	----
8	**21**	*n*-BuLi	53%	100% **32b**	----
9	**21**	*sec*-BuLi	52%	100% **32c** [b]	----
10	**21**	PheLi	78%	100% **32d**	----

[a] after purification [b] *ca.* 1:1 mixture of two diastereomers according to 400 MHz ^{1}H-NMR [c] crude product.

Scheme 5



30a-d **34a-d**

a: R= Me **b**: R= n-Bu **c**: R= s-Bu **d**: R= Ph

concave and *convex* face of the tricyclodecadienone molecule, but due to the newly formed stereogenic center in the *sec*-butyl group in both **30c** and **32c**.

Structural assignments

The gross structures of the 1,2-addition products were again deduced from their spectral data. After having assigned all resonances in the ^{1}H-NMR spectra applying selective decoupling experiments, the configuration at C_3 in the 1,2-adducts was further ascertained by NOE experiments (Table 5) and chemical transformations (Scheme 5). In Table 5 the interatomic distances to the nearest proton of the methyl group, calculated[18,19] for the conceivable alcohols from 1,2-addition of MeLi or MeMgI to either **12** or **21**, are

Table 5. Observed NOE-effects in **30a**-**33a**.

	distance between H_x and the nearest H of the methyl group (in Å) [a,18,19].			
H_x	**30a**	**31a**	**32a**	**33a**
H_1	3.9	2.8	3.8	2.5
H_2	2.5	3.2	2.5	3.3
H_3	----	----	----	----
H_4	2.8	2.8	2.8	2.8
H_5	4.1	4.6	4.2	4.5
H_6	3.3	4.9	3.5	4.9
H_7	>5	>5	>5	4.9
H_8	>5	4.2	>5	>5
H_9	>5	2.3	>5	4.8
H_{10a}	>5	5.0	5.0	2.4
H_{10s}	4.9	4.9	>5	3.7
OH	3.4	3.4	2.5	2.4

[a] A NOE-effect is expected for protons within 3 Å of the nearest proton of the methyl group. If a NOE-effect is indeed observed, the corresponding distance is underlined.

collected. As alcohols **31a** and **33a** are not available, NOE data could only be obtained for the isolated alcohols **30a** and **32a**. These agree nicely with the predictions based on calculated distances (Table 5).

The *endo*-configuration of the alcohol group in **30a-d** was proven independently by reacting these alcohols with *N*-bromosuccinimide (NBS) in tetrachloromethane (Scheme 5). These alcohols gave the expected[29] α-bromo ethers **34a-d** in almost quantitative yield. This intramolecular reaction is only feasible for *endo*-alcohols.

CONCLUDING REMARKS

Both 1,2- and 1,4-additions of organometallic compounds to parent *endo*- or *exo*-tricyclodecadienones **12** or **21** invariably occur stereospecifically from the *convex* face of the tricyclic skeleton, indicating that the selectivity of these additions is completely governed by the steric bulk of the norbornene moiety annelated to the cyclopentenone ring system, irrespective of the mode of annelation. Hence, *endo*- and *exo*-tricyclodecadienone **12** and **21** both can be applied for stereo- and enantioselective synthesis of

cyclopentenoids and related compounds, using the synthetic strategy depicted in Scheme 1. For tricyclic ester **18**, however, a diminished stereocontrol of *convex* over *concave* 1,4-addition is observed, contrary to our preliminary report[4c].

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 Bruker double focussing VG 7070E mass spectrometer was used. Elemental analyses were performed on a Carlo Eban Instruments CHNS-O 1108 Elemental analyzer. 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. All solvents used were dried and distilled according to standard procedures.

General procedures

A: Reactions of **12**, **18** *and* **21** *with MeMgI/CuCl.*
A solution of MeI (*ca.* 5-6 mmol) in dry ether is gradually added under a nitrogen atmosphere to activated magnesium (*ca.* 6-7 mmol), covered with dry ether. If necessary, the mixture is cooled to gentle reflux. After the magnesium has disappeared almost completely, dry CuCl (*ca.* 20 mg) is added to the turbid white mixture. The resulting green-yellow mixture is cooled to 0 °C in an ice-bath and a solution of the starting material in approximately 10 ml ether is added dropwise over a period of 5-10 minutes. Next, the mixture is stirred at room temperature until the reaction is complete according to cap. GC (± 2 hrs.). The crude reaction mixture is quenched with an aqueous solution of ammonium chloride and the aqueous phase extracted with ether (2x). The combined organic solutions are washed with water (3x), dried ($MgSO_4$), filtered and the solvent evaporated under reduced pressure. Analytical samples are obtained by crystallization or flash chromatography.

B: Reactions of **12**, **18** *and* **21** *with* R_2CuLi.
A solution of RLi (*ca.* 4 equiv.) in hexane is gradually added under a nitrogen atmosphere to a suspension of dry CuI (*ca.* 2 equiv.) in dry ether at 0 °C. After stirring the mixture for 15 minutes at 0 °C a solution of the starting material (1-2 mmol) in ether (10 ml) is gradually added. Next, the mixture is stirred at room temperature until the reaction is complete according to cap. GC (± 2 hrs.). After work-up according to standard procedures (*cf.* general procedure A), analytical samples are obtained by crystallization or flash chromatography.

C: Reactions of **12** *and* **21** *with MeMgI.*
A solution of MeI (*ca.* 4 equiv.) in dry ether (10 ml) is gradually added under a nitrogen atmosphere to activated magnesium turnings, covered with dry ether. If necessary, the mixture is cooled to gentle reflux. After the magnesium has disappeared almost completely, the turbid white mixture is cooled to 0 °C and a solution of the starting material (2-3 mmol) in ether (10 ml) is gradually added. Next, the mixture is stirred at room temperature until the reaction is complete according to cap. GC (± 2 hrs.). After work-up according to standard procedures (*cf.* general procedure A), analytical samples are obtained by crystallization or flash chromatography.

D: Reactions of **12** *and* **21** *with RLi.*
A solution of RLi in hexane (*ca.* 2 equiv.) is gradually added under a nitrogen atmosphere to a solution of the starting material (1-3 mmol) in dry ether (20 ml) at -78 °C. After stirring the mixture for 2 hours at -78 °C complete conversion is achieved. After work-up according to standard procedures (*cf.* general procedure A), analytical samples are obtained by crystallization or flash chromatography.

E: Reactions of tricyclic endo*-alcohols* **30a-d** *with N-bromosuccinimide (NBS).*
N-bromosuccinimide (*ca.* 1.5-3 equiv.) is added to a solution of *endo*-alcohols **30a-d** (0.5-1.0 mmol) in CCl_4 (10 ml) and the resulting mixture is stirred at room temperature until the reaction is complete according to cap. GC. Subsequently, the crude reaction mixture is filtered to remove the insoluble NBS and succinimide. After removal of the solvent by evaporation under reduced pressure the α-bromo ethers **34a-d** are obtained. Analytical samples are obtained by flash chromatography (**34a-c**) or crystallization (**34d**).

exo-5-*Methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **13a**
Following general procedure A [Mg (173 mg, 7.1 mmol), MeI (420 µl of a 16.1 M solution in ether, 6.8 mmol), CuCl], starting material **12** (504 mg, 3.5 mmol), gave, after work-up, 536 mg of a yellow oil, consisting of 3% **30a** and 97% **13a** (cap. GC). Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**13a**)= 0.45) yielded 436 mg (77%) **13a** as a colorless oil.
Following general procedure B [MeLi (1.25 ml of a 1.6 M solution in hexane, 2.0 mmol), CuI (197 mg, 1.0 mmol)], starting material **12** (99 mg, 0.68 mmol), gave, after work-up, 108 mg of a yellow oil. Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**13a**)= 0.45) yielded 92 mg (84%) **13a** as a colorless oil.
13a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.16 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), 6.12 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.18-3.16 (m, 1H, H_1), 3.07-3.05 (m, 1H, H_7), 2.95 A of AB (ddd, $J_{2,6}$=9.4 Hz, $J_{1,2}$=4.7 Hz, $J_{2,4x}$=1.4 Hz, 1H, H_2), 2.56 B of AB (dt, $J_{5,6}\approx J_{6,7}\approx$3.8 Hz, 1H, H_6), 2.23 A of AB (dd, $J_{4n,4x}$=20.1 Hz, $J_{4n,5}$=10.6 Hz, 1H, H_{4n}), 1.89-1.83 (m, 2H, H_{4x} and H_5), 1.54 A of AB (dt, $J_{10a,10s}$=8.2 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}), 1.40 B of AB (dt, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10s}\approx J_{7,10s}\approx$1.5 Hz, 1H, H_{10a} or H_{10s}), 1.09 (d, $J_{5,CH3}$=6.9 Hz, 3H, $-CH_3$). IR ($CHCl_3$): υ 3060 (C-H, unsat.), 3030-2770 (C-H, sat.), 1715 (C=O) cm^{-1}. CI/MS: *m/e* (%) 163 (2,M^++1), 97 (100,$-C_5H_6$), 81 (6,M^+-C_5H_6,$-CH_3$), 66 (88,$C_5H_6^+$). EI/HRMS *m/e*: 162.1044 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

exo-5-*n-Butyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **13b**
Following general procedure B [*n*-BuLi (4.30 ml of a 1.6 M solution in hexane, 6.9 mmol), CuI (676 mg, 3.6 mmol)], starting material **12** (250 mg, 1.7 mmol), gave, after work-up, 339 mg (quant.) **13b** as a colorless oil (purity > 99%, cap. GC).
13b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.15-6.14 (m, 2H, H_8 and H_9), 3.18-3.16 (m, 1H, H_1), 3.03-3.01 (m, 1H, H_7), 2.93 A of AB (ddd, $J_{2,6}$=9.5 Hz, $J_{1,2}$= 4.7 Hz, $J_{2,4x}$=1.9 Hz, 1H, H_2), 2.62 B of AB (dt, $J_{5,6}\approx J_{6,7}\approx$4.1 Hz, 1H, H_6), 2.21 A of AB (dd, $J_{4n,4x}$=18.5 Hz, $J_{4n,5}$=9.0 Hz, 1H, H_{4n}), 1.94 B of AB (ddd, $J_{4x,5}$=7.0 Hz, 1H, H_{4x}), 1.71-1.64 (m, 1H, H_5), 1.55 A of AB (d, $J_{10a,10s}$=8.1 Hz, 1H, H_{10a} or H_{10s}), 1.42 B of AB (d, 1H, H_{10a} or H_{10s}), 1.46-1.25 (m, 6H, $-CH_2CH_2CH_2CH_3$), 0.91 (t, $J_{CH2,CH3}$=6.8 Hz, 3H, $-CH_2CH_2CH_2CH_3$). IR (CCl_4): υ 3060 (C-H, unsat.), 3030-2760 (C-H, sat.), 1725 (C=O) cm^{-1}. CI/MS: *m/e* (%) 205 (7,M^++1), 147 (3,M^+-*n*-Bu), 139 (100,$-C_5H_6$), 81 (9,M^+-C_5H_6,-*n*-Bu), 66 (99,$C_5H_6^+$), 57 (2,*n*-Bu^+). EI/HRMS *m/e*: 204.1513 (calc. for $C_{14}H_{20}O$ (M^+): 204.1514).

exo-5-*Phenyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **13c**
Following general procedure B [PheLi (3.60 ml of a 2.0 M solution in hexane, 7.2 mmol, the use of exactly two equiv. of PheLi gave poor yields), CuI (412 mg, 2.2 mmol)], starting material **12** (201 mg, 1.4 mmol), gave, after work-up, 592 mg of a dark yellow oil. Flash chromatography (hexane:ethyl acetate = 10:1, R_f(biphenyl)= 0.79, R_f(**13c**)= 0.31) yielded 160 mg (1.0 mmol) biphenyl and 285 mg (93%) **13c** as a slightly yellow oil.
13c: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 2H, H_{ortho}), 7.25-7.16 (m, 3H, H_{meta} and H_{para}), 6.30 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.26 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.25-3.23 (m, 1H, H_1 or H_7), 3.15 (m, 1H, H_1 or H_7), 3.13 A of AB (ddd, $J_{1,2}$=4.6 Hz, $J_{2,4x}$=1.6 Hz, 1H, H_2), 3.02 B of AB (dt, $J_{2,6}$=9.5 Hz, $J_{5,6}\approx J_{6,7}\approx$4.3 Hz, 1H, H_6), 2.95-2.89 (m, 1H, H_5), 2.52 A of AB (dd, $J_{4n,4x}$=18.4 Hz, $J_{4n,5}$=9.1 Hz, 1H, H_{4n}), 2.43 B of AB (ddd, $J_{4x,5}$=7.7 Hz, 1H, H_{4x}), 1.61 A of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10a} or H_{10s}), 1.44 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CCl_4): υ 3120-3010 (C-H, unsat.), 3010-2820 (C-H, sat.), 1730 (C=O), 700 (phenyl, mono-subst.) cm^{-1}. CI/MS: *m/e* (%) 225 (2,M^++1), 159 (99,$-C_5H_6$), 147 (3,M^+-C_6H_5), 119 (7,M^+-C_6H_5,-CO), 81 (6,M^+-C_6H_5,-C_5H_6), 77 (13,$C_6H_5^+$), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 224.1200 (calc. for $C_{16}H_{16}O$ (M^+): 224.1201).

endo-5-*Methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **14a**[17]
At 0 °C, *tert*-butyl alcohol (817 mg, 11.0 mmol) was gradually added to a suspension of lithium aluminum hydride (130 mg, 3.4 mmol) in ether (20 ml). After all the *tert*-butyl alcohol had been added the mixture was stirred for another hour at room temperature. Next, a solution of starting material **24** (262 mg, 1.6 mmol) in ether (10 ml) was gradually added. After 5 hours the reaction was quenched by adding water (10 ml). Subsequently, the mixture was acidified to neutral pH by adding 3% HCl and the organic and aqueous layers separated. The remaining aqueous phase was extracted once more with ether. The combined organic phases were washed three times with water and dried ($MgSO_4$). Filtration and evaporation of the solvent under reduced pressure, gave 277 mg of a yellow oil, consisting primarily of 1,2 and 1,4-reduced product. After flash chromatography (Al_2O_3, hexane:ethyl acetate = 2:1, R_f(**14a**)= 0.70), 121 mg (47%) **14a** and 61 mg (24%) 1,2-reduced product were isolated.
14a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.21 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{7,8}$=2.8 Hz, 1H, H_8), 6.01 B of AB (dd, $J_{1,9}$=2.9 Hz, 1H, H_9), 3.17 (bs, 1H, H_1), 3.04 (bs, 1H, H_7), 2.92 (bs, 2H, H_2 and H_6), 2.43-2.36 (m, 1H, H_5), 2.10 A of AB (dd, $J_{4n,4x}$=18.4 Hz, $J_{4x,5}$=9.1 Hz, 1H, H_{4x}), 1.69 B of AB (dd, $J_{4n,5}$=12.8 Hz, 1H, H_{4n}), 1.53 A of AB (d, $J_{10a,10s}$=8.1 Hz, 1H, H_{10a} or H_{10s}), 1.38 B of AB (d, 1H, H_{10a} or H_{10s}), 1.11 (d, $J_{5,CH3}$=6.9 Hz, 3H,

-CH_3). IR (CCl_4): υ 3060 (C-H, unsat.), 3050-2770 (C-H, sat.), 1730 (C=O) cm^{-1}. CI/MS: *m/e* (%) 163 (8,M^++1), 135 (10,-CO), 97 (96,-C_5H_6), 81 (14,M^+-C_5H_6,-CH_3), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 162.1043 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

Ethyl exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate* **19a** and *ethyl* endo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate* **20a**

Following general procedure A [Mg (143 mg, 5.9 mmol), MeI (360 µl of a 16.1 M solution in ether, 5.8 mmol), CuCl], starting material **18** (542 mg, 2.5 mmol), gave, after work-up, 463 mg (80%) of a yellow oil, consisting of 53% **19a** and 13% **20a** (cap. GC).

Following general procedure B [MeLi (5.70 ml of a 1.6 M solution in hexane, 9.1 mmol), CuI (874 mg, 4.6 mmol)], starting material **18** (496 mg, 2.3 mmol), gave, after work-up, 468 mg of a yellow oil, consisting of 63% **19a** and 21% **20a** (cap. GC). Flash chromatography (hexane:ethyl acetate = 98:2) yielded 278 mg (52%) **19a** and 41 mg (8%) **20a**, both as a colorless oil.

19a: ^{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), 6.20 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 4.24 (q, $J_{CH2,CH3}$=7.1 Hz, 2H, -OC$\underline{H}_2$$CH_3$), 3.49-3.46 (m, 2H, H_6 and H_1 or H_7), 3.19-3.16 (m, 1H, H_1 or H_7), 2.31 A of AB (ddd, $J_{4n,4x}$=17.3 Hz, $J_{3,4x}$=10.7 Hz, $J_{4x,6}$=1.6 Hz, 1H, H_{4x}), 2.25 B of AB (dd, $J_{3,4n}$=7.9 Hz, 1H, H_{4n}), 2.09-1.99 (m, 1H, H_3), 1.69 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10a} or H_{10s}), 1.41 B of AB (d, 1H, H_{10a} or H_{10s}), 1.32 (t, 3H, -OCH_2C$\underline{H}_3$), 1.04 (d, $J_{3,CH3}$=7.0 Hz, 3H, -CH_3). IR ($CHCl_3$): υ 3060 (C-H, unsat.), 3030-2780 (C-H, sat.), 1720 (C=O, 2x), 1230 (C-O, ester) cm^{-1}. CI/MS: *m/e* (%) 235 (12,M^++1), 207 (8,-C_2H_4 or -CO), 189 (16,-C_2H_5OH), 169 (100,-C_5H_6), 141 (6,-C_2H_4 or -CO,-C_5H_6), 123 (22,-C_5H_6,-C_2H_5OH), 95 (12,M^+-C_5H_6,-$CO_2C_2H_5$), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 234.1263 (calc. for $C_{14}H_{18}O_3$ (M^+): 234.1256).

20a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.35 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$=3.1 Hz, 1H, H_9), 6.16 B of AB (dd, $J_{7,8}$=2.9 Hz, 1H, H_8), 4.24-4.16 (m, 2H, -OC$\underline{H}_2$$CH_3$), 3.49 (d, $J_{6,7}$=5.1 Hz, 1H, H_6), 3.46 (bs, 1H, H_1), 3.23-3.21 (m, 1H, H_7), 2.53-2.38 (m, 1H, H_3), 2.32 A of AB (ddd, $J_{4n,4x}$=18.4 Hz, $J_{3,4x}$=9.4 Hz, $J_{4x,6}$=1.5 Hz, 1H, H_{4x}), 1.84 B of AB (ddd, $J_{3,4n}$=11.9 Hz, $J_{4n,6}$=1.0 Hz, 1H, H_{4n}), 1.57 A of AB (d, $J_{10a,10s}$=8.7 Hz, 1H, H_{10a} or H_{10s}), 1.42 B of AB (d, 1H, H_{10a} or H_{10s}), 1.29 (t, $J_{CH2,CH3}$=7.1 Hz, 3H, -OCH_2C$\underline{H}_3$), 1.21 (d, $J_{3,CH3}$=6.9 Hz, 3H, -CH_3). IR (CCl_4): υ 3060 (C-H, unsat.), 3030-2780 (C-H, sat.), 1720 (C=O, 2x), 1225 (C-O, ester) cm^{-1}. CI/MS: *m/e* (%) 235 (8,M^++1), 207 (5,-C_2H_4 or -CO), 189 (16,-C_2H_5OH), 169 (100,-C_5H_6), 141 (13,-C_5H_6,-C_2H_4 or -CO), 123 (34,-C_5H_6,-C_2H_5OH), 95 (20,M^+-C_5H_6,-$CO_2C_2H_5$), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 234.1263 (calc. for $C_{14}H_{18}O_3$ (M^+): 234.1256).

Ethyl exo-3-*n-butyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate* **19b** and *ethyl* endo-3-*n-butyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate* **20b**

Following general procedure B [*n*-BuLi (2.80 ml of a 1.6 M solution in hexane, 4.5 mmol), CuI (370 mg, 1.9 mmol)], starting material **18** (209 mg, 0.96 mmol), gave, after work-up, 284 mg of a yellow oil, consisting of 83% **19b** and 11% **20b** (cap. GC). Flash chromatography (hexane:ethyl acetate = 10:1, R_f(**19b**)= 0.44, R_f(**20b**)= 0.36) yielded 162 mg (61%) **19b** and 36 mg (14%) **20b**, both as a colorless oil.

19b: ^{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), 6.18 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 4.24 (dq, $J_{CHa,CH3}$≈$J_{CHb,CH3}$≈7.2 Hz, 2H, -OC$\underline{H}_a$$\underline{H}_b$$CH_3$), 3.46 (bs, 1H, H_1), 3.40 (dd, $J_{6,7}$=4.6 Hz, $J_{4x,6}$=2.1 Hz, 1H, H_6), 3.16-3.14 (m, 1H, H_7), 2.40 A of AB (ddd, $J_{4n,4x}$=16.9 Hz, $J_{3,4x}$=12.5 Hz, 1H, H_{4x}), 2.24 B of AB (dd, $J_{3,4n}$=7.4 Hz, 1H, H_{4n}), 1.91-1.82 (m, 1H, H_3), 1.72 A of AB (d, $J_{10a,10s}$=8.7 Hz, 1H, H_{10a} or H_{10s}), 1.59-1.48 and 1.34-1.19 (2 m, 1H and 5H, -C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$$CH_3$), 1.42 B of AB (d, 1H, H_{10a} or H_{10s}), 1.32 (t, 3H, -OCH_2C$\underline{H}_3$), 0.88 (t, $J_{CH2,CH3}$=7.0 Hz, 3H, -$CH_2CH_2CH_2$C$\underline{H}_3$). IR (CCl_4): υ 3060 (C-H, unsat.), 3040-2770 (C-H, sat.), 1720 (C=O, 2x), 1225 (C-O, ester) cm^{-1}. EI/MS: *m/e* (%) 276 (1,M^+), 247 (1,-C_2H_5), 231 (3,-OC_2H_5), 211 (85,-C_5H_5), 183 (3,-C_5H_5,-C_2H_4 or -CO), 165 (13,-C_5H_6,-OC_2H_5), 137 (12,-C_5H_6,-$CO_2C_2H_5$), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 276.1729 (calc. for $C_{17}H_{24}O_3$ (M^+): 276.1725).

20b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.32 A of AB (bdd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 4.26-4.14 (m, 2H, -OC$\underline{H}_2$$CH_3$), 3.47 (bs, 1H, H_1), 3.45 (dd, $J_{6,7}$=5.1 Hz, $J_{4x,6}$=1.5 Hz, 1H, H_6), 3.22-3.19 (m, 1H, H_7), 2.40-2.27 AB (m, 2H, H_{4n} and H_{4x}), 1.93-1.77 (m, 2H, H_3 and 1H of -C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$$CH_3$), 1.58 A of AB (dt, $J_{10a,10s}$=8.8 Hz, $J_{1,10a}$≈$J_{7,10a}$ resp. $J_{1,10s}$≈$J_{7,10s}$≈1.5 Hz, 1H, H_{10a} or H_{10s}), 1.40 B of AB (d, 1H, H_{10a} or H_{10s}), 1.42-1.15 (m, 5H, 5H of -C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$$CH_3$), 1.29 (t, $J_{CH2,CH3}$=7.1 Hz, 3H, -OCH_2C$\underline{H}_3$), 0.90 (t, $J_{CH2,CH3}$=7.1 Hz, 3H, -$CH_2CH_2CH_2$C$\underline{H}_3$). IR (CCl_4): υ 3060 (C-H, unsat.), 3030-2790 (C-H, sat.), 1720 (C=O, 2x), 1230 (C-O, ester) cm^{-1}. EI/MS: *m/e* (%) 276 (1,M^+), 231 (3,-OC_2H_5), 211 (67,-C_5H_5), 183 (3,-C_5H_5,-C_2H_4 or -CO), 165 (11,-C_5H_6,-OC_2H_5), 137 (9,-C_5H_6,-$CO_2C_2H_5$), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 276.1726 (calc. for $C_{17}H_{24}O_3$ (M^+): 276.1725).

Ethyl exo-3-*phenyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate **19c** and *ethyl* endo-3-*phenyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*one*-2-*carboxylate **20c***

Following general procedure B [PheLi (2.70 ml of a 2.0 M solution in hexane, 5.4 mmol, the use of exactly two equiv. of PheLi gave poor yields), CuI (303 mg, 1.6 mmol)], starting material **18** (209 mg, 0.96 mmol), gave, after work-up, 650 mg of a dark yellow oil. Flash chromatography (hexane:ethyl acetate = 10:1, R_f(biphenyl)= 0.74, R_f(**19c**)=R_f(**20c**)= 0.13) yielded 177 mg (1.2 mmol) biphenyl and 259 mg (92%) of a mixture of **19c** and **20c** (ratio **19c**:**20c** = 1:2, according to 400 MHz ^{1}H-NMR) as a yellow oil.

19c and **20c** (1:2 mixture): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.13 (m, 2x5H, $H_{arom.}$ of **19c** and **20c**), 6.42 (pt, J≈1.9 Hz, 2H, H_8 and H_9 of **19c**), 6.12 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9 of **20c**), 5.79 B of AB (bdd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9 of **20c**), 4.35-4.28 (dq, J_{CH_a,CH_3}≈J_{CH_b,CH_3}≈7.1 Hz, 2H, -OCH_aH_bCH_3 of **20c**), 3.97 (dd, $J_{3,4n}$=12.3 Hz, $J_{3,4x}$=9.7 Hz, 1H, H_3 of **20c**), 3.67 A of AB (dq, J_{CH_a,CH_b}=10.7 Hz, J_{CH_a,CH_3}=7.2 Hz, 1H, -OCH_aH_bCH_3 of **19c**), 3.61-3.58 (m, 1H, H_1 or H_7 of **20c**), 3.58 B of AB (dq, J_{CH_b,CH_3}=7.2 Hz, 1H, -OCH_aH_bCH_3 of **19c**), 3.39 (d, $J_{6,7}$=5.0 Hz, 1H, H_6 of **20c**), 3.28-3.24 (m, 4H, H_1, H_3, H_6 and H_7 of **19c**), 3.21-3.19 (m, 1H, H_1 or H_7 of **20c**), 3.05 A of AB (ddd, $J_{4n,4x}$=17.0 Hz, $J_{3,4x}$=11.4 Hz, $J_{4x,6}$=2.2 Hz, 1H, H_{4x} of **19c**), 2.68 A of AB (dd, $J_{4n,4x}$=18.3 Hz, 1H, H_{4n} of **20c**), 2.59 B of AB (ddd, $J_{4x,6}$=1.3 Hz, 1H, H_{4x} of **20c**), 2.47 B of AB (dd, $J_{3,4n}$=7.9 Hz, 1H, H_{4n} of **19c**), 1.75 A of AB (d, $J_{10a,10s}$=8.9 Hz, 1H, H_{10a} or H_{10s} of **19c**), 1.55 A of AB (d, $J_{10a,10s}$=8.9Hz, 1H, H_{10a} or H_{10s} of **20c**), 1.49 B of AB (d, 1H, H_{10a}or H_{10s} of **19c**), 1.44 B of AB (d, 1H, H_{10a} or H_{10s} of **20c**), 1.34 (t, 3H, -OCH_2CH_3 of **20c**), 0.86 (t, 3H, -OCH_2CH_3 of **19c**). IR (CCl_4): υ 3100-3010 (C-H, unsat.), 3010-2780 (C-H, sat.), 1725 (C=O, 2x), 1225 (C-O, ester), 700 (phenyl, mono-subst.) cm^{-1}. CI/MS: *m/e* (%) 297 (16,M^++1), 251 (10,-C_2H_5OH), 231 (98,-C_5H_6), 230 (100,M^+-C_5H_6), 223 (15,M^+-$CO_2C_2H_5$), 202 (5,-C_5H_6,-C_2H_5), 185 (22,-C_5H_6,-C_2H_5OH), 157 (14,M^+-C_5H_6,-$CO_2C_2H_5$), 77 (5,$C_6H_5^+$), 66 (54,$C_5H_6^+$). EI/HRMS *m/e*: 296.1414 (calc. for $C_{19}H_{20}O_3$ (M^+): 296.1412).

exo-5-*Methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **22a**

Following general procedure A [Mg (266 mg, 10.9 mmol), MeI (630 μl of a 16.1 M solution in ether, 10.1 mmol), CuCl], starting material **21** (500 mg, 3.4 mmol), gave, after work-up, 468 mg (84%) of a yellow oil, consisting of 4% **32a** and 96% **22a** (cap. GC). Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**22a**)= 0.43) yielded 314 mg (56%) **22a** as a colorless oil.

Following general procedure B [MeLi (1.20 ml of a 1.6 M solution in hexane, 1.9 mmol), CuI (196 mg, 1.0 mmol)], starting material **21** (100 mg, 0.68 mmol), gave, after work-up, 90 mg (82%) of a yellow oil. Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**22a**)= 0.43) yielded 60 mg (54%) **22a** as a colorless oil.

22a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.10 (bs, 1H, H_1), 2.79 (bs, 1H, H_7), 2.62 A of AB (dd, $J_{4n,4x}$=17.8 Hz, $J_{4n,5}$=7.9 Hz, 1H, H_{4n}), 2.32 A of AB (bd, $J_{2,6}$=8.7 Hz, 1H, H_2), 2.23 B of AB (ddd, $J_{4x,5}$=10.2 Hz, $J_{2,4x}$=1.8 Hz, 1H, H_{4x}), 1.94 B of AB (bt, $J_{2,6}$≈$J_{5,6}$, 1H, H_6), 1.90-1.81 (m, 1H, H_5), 1.42 A of AB (dt, $J_{10a,10s}$=9.3 Hz, $J_{2,10a}$≈$J_{6,10a}$≈1.5 Hz, 1H, H_{10a}), 1.24 B of AB (d, 1H, H_{10s}), 1.19 (d, $J_{5,CH3}$=6.8 Hz, 3H, -CH_3). IR ($CHCl_3$): υ 3060 (C-H, unsat.), 3030-2780 (C-H, sat.), 1720 (C=O) cm^{-1}. EI/MS: *m/e* (%) 162 (3,M^+), 97 (92,-C_5H_5), 81 (24,-C_5H_6,-CH_3), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 162.1044 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

exo-5-*n-Butyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **22b**

Following general procedure B [*n*-BuLi (4.30 ml of a 1.6 M solution in hexane, 6.9 mmol), CuI (666 mg, 3.5 mmol)], starting material **21** (261 mg, 1.8 mmol), gave, after work-up, 328 mg of a yellow oil. Flash chromatography (hexane:ethyl acetate = 5:1, R_f(**22b**)= 0.59) yielded 299 mg (83%) **22b** as a colorless oil.

22b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.10 (bs, 1H, H_1), 2.76 (bs, 1H, H_7), 2.60 A of AB (dd, $J_{4n,4x}$=17.7 Hz, $J_{4n,5}$=8.5 Hz, 1H, H_{4n}), 2.29 A of AB (bd, $J_{2,6}$≈8.2 Hz, 1H, H_2), 2.25 B of AB (ddd, $J_{4x,5}$=10.5 Hz, $J_{2,4x}$=1.9 Hz, 1H, H_{4x}), 1.98 B of AB (bt, $J_{2,6}$≈$J_{5,6}$, 1H, H_6), 1.95-1.30 (m, 7H, H_5 and -CH_2CH_2CH_2CH_3), 1.42 A of AB (dt, $J_{10a,10s}$=9.1 Hz, $J_{2,10a}$≈$J_{6,10a}$≈1.5 Hz, 1H, H_{10a}), 1.23 B of AB (d, 1H, H_{10s}), 0.92 (t, $J_{CH2,CH3}$=6.9 Hz, 3H, -$CH_2CH_2CH_2CH_3$). IR (CCl_4): υ 3060 (C-H, unsat.), 3030-2750 (C-H, sat.), 1725 (C=O) cm^{-1}. CI/MS: *m/e* (%) 205 (4,M^++1), 147 (1,M^+-*n*-Bu), 139 (100,-C_5H_6), 81 (5,M^+-C_5H_6,-*n*-Bu), 66 (100,$C_5H_6^+$), 57 (1,*n*-Bu^+). CI/HRMS *m/e*: 139.1124 (calc. for $C_9H_{15}O$ (M^++1-C_5H_6): 139.1123).

exo-5-*Phenyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **22c**

Following general procedure B [PheLi (3.00 ml of a 2.0 M solution in hexane, 6.0 mmol, the use of exactly two equiv. of PheLi gave poor yields), CuI (410 mg, 2.2 mmol)], starting material **21** (207 mg, 1.4 mmol), gave, after work-up, 447 mg of a dark yellow oil. Flash chromatography (hexane:ethyl acetate = 10:1, R_f(biphenyl)= 0.72, R_f(**22c**)= 0.41) yielded 148 mg (0.96 mmol) biphenyl and 238 mg (79%) **22c** as a slightly yellow oil.

22c: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H, H_{ortho}), 7.28-7.24 (m, 3H, H_{meta} and H_{para}), 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), 6.14 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.20 (bs, 1H, H_1 or H_7), 2.95-2.80 (m, 4H, H_1, H_{4n}, H_{4x}, H_5 and H_7), 2.50 A of AB (bd, $J_{2,6}$=9.1 Hz, 1H, H_2), 2.43 B of AB (bt, $J_{2,6}$≈$J_{5,6}$, 1H, H_6), 1.52 A of AB (dt, $J_{10a,10s}$=9.3 Hz, $J_{2,10a}$≈$J_{6,10a}$≈1.4 Hz, 1H, H_{10a}), 1.39 B of AB (d, 1H, H_{10s}). IR (CCl_4): υ 3120-3005 (C-H, unsat.), 3005-2840 (C-H, sat.), 1735 (C=O), 700 (phenyl, mono-subst.) cm^{-1}. CI/MS: *m/e* (%) 225 (1,M^++1), 159 (100,-C_5H_6), 147 (2,M^+-C_6H_5), 119 (12,M^+-C_6H_5,-CO), 81 (3,M^+-C_5H_6,-C_6H_5), 77 (6,$C_6H_5^+$), 66 (89,$C_5H_6^+$). EI/HRMS *m/e*: 224.1200 (calc. for $C_{16}H_{16}O$ (M^+): 224.1201).

endo-5-*Methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **23a**[17]
At 0 °C, *tert*-butyl alcohol (844 mg, 11.4 mmol) was gradually added to a suspension of lithium aluminum hydride (135 mg, 3.6 mmol) in ether (20 ml). After all the *tert*-butyl alcohol had been added the mixture was stirred for another hour at room temperature. Next, a solution of starting material **25** (249 mg, 1.6 mmol) in ether (10 ml) was gradually added. After 5 hours the reaction was quenched by adding water (10 ml). Subsequently, the mixture was acidified to neutral pH by adding 3% HCl and the organic and aqueous layers separated. The remaining aqueous phase was extracted once more with ether. The combined organic phases were washed three times with water and dried ($MgSO_4$). After filtration and evaporation of the solvent under reduced pressure, 225 mg of a yellow oil, consisting primarily of 1,2 and 1,4-reduced product was isolated. After flash chromatography (Al_2O_3, hexane:ethyl acetate = 2:1, R_f(**23a**)= 0.78), 111 mg (43%) **23a** was obtained.
23a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.23-6.21 A of AB (m, 1H, H_8 or H_9), 6.19-6.17 B of AB (m, 1H, H_8 or H_9), 3.04 (bs, 2H, H_1 and H_7), 2.63-2.52, 2.33-2.27 and 2.17-2.11 (3 m, 2H, 2H and 1H, H_2, H_{4n}, H_{4x}, H_5 and H_6), 1.37 A of AB (dt, $J_{10a,10s}$=9.3 Hz, $J_{2,10a}$≈$J_{6,10a}$≈1.5 Hz, 1H, H_{10a}), 1.29 B of AB (d, 1H, H_{10s}), 1.16 (d, $J_{5,CH3}$=6.7 Hz, 3H, -CH_3). IR (CCl_4): υ 3060 (C-H, unsat.), 3030-2780 (C-H, sat.), 1725 (C=O) cm^{-1}. CI/MS: *m/e* (%) 163 (5,M^++1), 135 (2,-CO), 97 (95,-C_5H_6), 81 (4,M^+-C_5H_6,-CH_3), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 162.1044 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

Ethyl exo-8,9-*epoxy*-exo-3-*methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*decan*-5-*one*-2-*carboxylate* **27**
Prior to use *meta*-chloroperbenzoic acid (193 mg, ± 0.78 mmol) was dissolved in dichloromethane (20 ml) and dried on $MgSO_4$. The solution was filtered and the filtrate added to tricyclic ester **19a** (129 mg, 0.55 mmol) and the resulting mixture stirred at room temperature until the reaction was complete according to cap. GC. The organic phase was washed with 2% sodium pyrosulfite in water, an aqueous solution of sodium bicarbonate and finally with water (2x). The aqueous phases were extracted once more with dichloromethane and the combined organic phases dried ($MgSO_4$) and filtered. After removal of the solvent under reduced pressure 155 mg crude product was obtained. Flash chromatography yielded 97 mg (71%) **27** as a colorless oil, which solidified on standing.
27: m.p.: 30-33 °C (*n*-pentane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.23 (q, $J_{CH2,CH3}$=7.1 Hz, 2H, -OCH_2CH_3), 3.37 (dd, $J_{6,7}$=5.1 Hz, $J_{4x,6}$=1.0 Hz, 1H, H_6), 3.31 A of AB (bd, $J_{8,9}$≈3.1 Hz, 1H, H_8 or H_9), 3.29 B of AB (bd, 1H, H_8 or H_9), 3.16 (d, $J_{1,9}$=1.5 Hz, 1H, H_1), 2.89-2.87 (m, 1H, H_7), 2.59-2.41 (m, 3H, H_{4n}, H_{4x} and H_3), 1.60 A of AB (d, $J_{10a,10s}$=10.4 Hz, 1H, H_{10s}), 1.32 (t, 3H, -OCH_2CH_3), 1.08 (d, $J_{3,CH3}$=6.5 Hz, 3H, -CH_3), 0.78 B of AB (d, 1H, H_{10a}). IR (CCl_4): υ 3030-2780 (C-H, sat.), 1725 (C=O, 2x), 1245 and 1215 (C-O, ester), 865 (C-O, epoxide) cm^{-1}. CI/MS: *m/e* (%): 251 (5,M^++1), 222 (6,-C_2H_5), 205 (6,-C_2H_5OH), 191 (3,-OC_2H_5,-CH_3), 177 (18,M^+-$CO_2C_2H_5$), 169 (17,-C_5H_6O), 141 (5,-C_5H_6O,-C_2H_4 or -CO), 81 (100,$C_5H_5O^+$). EI/HRMS *m/e*: 250.1207 (calc. for $C_{14}H_{18}O_4$ (M^+): 250.1205).

exo-3-*Methyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **30a**
Following general procedure C [Mg (97 mg, 4.0 mmol), MeI (590 mg, 4.2 mmol)], starting material **12** (176 mg, 1.2 mmol), gave, after work-up, 177 mg of a yellow oil, consisting of 86% **30a** and 6% **13a** (cap. GC). Flash chromatography (hexane:ethyl acetate = 5:1, R_f(**30a**)= 0.41) yielded 148 mg (76%) **30a** as a white solid.
Following general procedure D [MeLi (2.40 ml of a 1.6 M solution in hexane, 3.8 mmol)], starting material **12** (471 mg, 3.2 mmol), gave, after work-up, 397 mg of a yellow oil. Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**30a**)= 0.51) yielded 270 mg (53%) **30a** as a white solid.
30a: m.p.: 46-48 °C (*n*-pentane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.18 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 5.87 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 5.48-5.44 (m, 2H, H_4 and H_5), 3.33-3.31 A of AB (m, $J_{2,6}$≈7.8 Hz, $J_{6,7}$≈4.3 Hz, $J_{4,6}$≈$J_{5,6}$≈1.5 Hz, 1H, H_6), 2.94 (bs, 1H, H_1 or H_7), 2.91-2.89 (m, 1H, H_1 or H_7), 2.59 B of AB (dd, $J_{1,2}$=4.2 Hz, 1H, H_2), 1.58 A of AB (dt, $J_{10a,10s}$=8.1 Hz, $J_{7,10a}$ resp. $J_{7,10s}$=1.8 Hz, 1H, H_{10a} or H_{10s}), 1.43-1.41 (m, 2H, H_{10a} or H_{10s} and -OH), 1.33 (s, 3H, -CH_3). IR (CCl_4): υ 3605 (free -OH), 3650-3120 (H-bonded -OH), 3050 (C-H, unsat.), 3020-2790 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 162 (3,M^+), 145 (100,-OH), 129 (19,-H_2O,-CH_3), 96 (4,-C_5H_6), 66 (2,$C_5H_6^+$). EI/HRMS *m/e*: 162.1045 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

exo-3-*n-Butyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **30b**
Following general procedure D [*n*-BuLi (0.90 ml of a 1.6 M solution in hexane, 1.4 mmol)], starting material

12 (106 mg, 0.73 mmol), gave, after work-up, 145 mg of a yellow oil. Flash chromatography (hexane:ethyl acetate = 4:1, R_f(**30b**)= 0.42) yielded 116 mg (78%) **30b** as a colorless oil.
30b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.18 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.7 Hz, 1H, H_8 or H_9), 5.85 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 5.50 A of AB (dd, $J_{4,5}$=5.7 Hz, $J_{4,6}$ resp. $J_{5,6}$=2.0 Hz, 1H, H_4 or H_5), 5.44 B of AB (dd, $J_{4,6}$ resp. $J_{5,6}$=1.5 Hz, 1H, H_4 or H_5), 3.28-3.25 A of AB (m, 1H, H_6), 2.90-2.88 (m, 2H, H_1 and H_7), 2.62 B of AB (dd, $J_{2,6}$=7.9 Hz, $J_{1,2}$=4.1 Hz, 1H, H_2), 1.59-1.30 (m, 9H, H_{10a}, H_{10s}, $-CH_2CH_2CH_2CH_3$ and -OH), 0.92-0.89 (m, 3H, $-CH_2CH_2CH_2CH_3$). IR (CCl_4): υ 3600 (free -OH), 3650-3080 (H-bonded -OH), 3040 (C-H, unsat.), 3010-2780 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 204 (13,M^+), 187 (100,-OH), 147 (20,-*n*-Bu), 144 (27,-C_3H_7,-OH), 138 (8,-C_5H_6), 129 (31,-*n*-Bu,-H_2O), 121 (32,-C_5H_6,-OH), 95 (51,-C_5H_6,-C_3H_7), 81 (15,-C_5H_6,-*n*-Bu), 66 (21,$C_5H_6^+$), 57 (11,*n*-Bu^+), 43 (7,$C_3H_7^+$). EI/HRMS *m/e*: 204.1516 (calc. for $C_{14}H_{20}O$ (M^+): 204.1514).

exo-3-*sec-Butyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **30c**
Following general procedure D [*n*-BuLi (1.00 ml of a 1.4 M solution in hexane, 1.4 mmol)], starting material **12** (101 mg, 0.69 mmol), gave, after work-up, 145 mg of a brown oil. Flash chromatography (hexane:ethyl acetate = 98:2, R_f(**30c**)= 0.52) yielded 101 mg (73%) of an approximately 1:1 mixture of two diastereomers of **30c** as a colorless oil.
30c (two diastereomers, ratio ≈ 1:1 according to 400 MHz ^{1}H-NMR): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19-6.18 A of AB (m, 1H, H_8 or H_9), 5.86 B of AB (bdd, $J_{8,9}$≈5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$≈3.1 Hz, 1H, H_8 or H_9), 5.55 resp. 5.54 A of AB (dd, $J_{4,5}$=5.6 Hz, $J_{4,6}$ resp. $J_{5,6}$=2.2 Hz, 1H, H_4 or H_5), 5.44 resp. 5.42 B of AB (dd, $J_{4,6}$ resp. $J_{5,6}$=1.8 Hz, 1H, H_4 or H_5), 3.22-3.18 (m, 1H, H_6), 2.86 (bs, 2H, H_1 and H_7), 2.66 (dd, $J_{2,6}$=7.8 Hz, $J_{1,2}$=3.4 Hz, 1H, H_2) resp. 2.65 (dd, $J_{2,6}$=7.3 Hz, $J_{1,2}$=3.8 Hz, 1H, H_2), 1.76-1.58, 1.49-1.35 and 1.08-.86 (3m, 2H, 2H and 8H, $-CH(CH_3)CH_2CH_3$, H_{10a}, H_{10s} and -OH). IR (CCl_4): υ 3600 (free -OH), 3680-3100 (H-bonded -OH), 3045 (C-H, unsat.), 3020-2760 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 204 (11,M^+), 187 (89,-OH), 175 (6,-C_2H_5), 157 (37,-C_2H_5,-H_2O), 147 (99,-*s*-Bu), 138 (12,-C_5H_6), 129 (33,-*s*-Bu,-H_2O), 120 (41,-C_5H_6,-H_2O), 109 (100,-C_2H_5,-C_5H_6), 91 (20,-C_2H_5,-C_5H_6,-H_2O), 81 (30,-C_5H_6,-*s*-Bu), 66 (24,$C_5H_6^+$), 57 (19,*s*-Bu^+). EI/HRMS *m/e*: 204.1506 (calc. for $C_{14}H_{20}O$ (M^+): 204.1514)

exo-3-*Phenyl*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **30d**
Following general procedure D [PheLi (0.80 ml of a 2.0 M solution in hexane, 1.6 mmol)], starting material **12** (115 mg, 0.79 mmol), gave, after work-up, 194 mg of a yellow oil. Flash chromatography (hexane:ethyl acetate = 8:1, R_f(**30d**)= 0.81) yielded 129 mg (73%) **30d** as a white solid.
30d: m.p.: 65-66 °C (*n*-pentane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H, H_{ortho}), 7.34-7.30 (m, 2H, H_{meta}), 7.24-7.19 (m, 1H, H_{para}), 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), 5.96 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 5.73 A of AB (dd, $J_{4,5}$=5.5 Hz, $J_{4,6}$ resp. $J_{5,6}$=2.0 Hz, 1H, H_4 or H_5), 5.56 B of AB (dd, $J_{4,6}$ resp. $J_{5,6}$=1.6 Hz, 1H, H_4 or H_5), 3.48-3.44 (m, 1H, H_6), 3.03 (bs, 1H, H_1 or H_7), 2.96-2.94 (m, 1H, H_1 or H_7), 2.92 B of AB (dd, $J_{2,6}$=7.9 Hz, $J_{1,2}$=4.2 Hz, 1H, H_2), 1.82 (s, 1H, -OH), 1.62 A of AB (dt, $J_{10a,10s}$=8.2 Hz, $J_{?,10a}$ resp. $J_{?,10s}$=1.6 Hz, 1H, H_{10a} or H_{10s}), 1.43 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CCl_4): υ 3600 (free -OH), 3660-3120 (H-bonded -OH), 3120-3010 (C-H, unsat.), 3010-2820 (C-H, sat.), 700 (phenyl, mono-subst.) cm^{-1}. EI/MS: *m/e* (%) 224 (7,M^+), 207 (72,-OH), 158 (100,-C_5H_6), 147 (10,-C_6H_5), 142 (10,-C_5H_5,-OH), 129 (20,-C_6H_5,-H_2O), 77 (13,$C_6H_5^+$), 66 (8,$C_5H_6^+$). Found: C 85.56, H 7.23 (calc. for $C_{16}H_{16}O$: C 85.68, H 7.19).

exo-3-*Methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **32a**
Following general procedure C [Mg (329 mg, 13.5 mmol), MeI (1.92 g, 13.5 mmol)], starting material **21** (490 mg, 3.4 mmol), gave, after work-up, 493 mg of a yellow oil, consisting of 63% **32a** and 32% **22a** (cap. GC). Flash chromatography (hexane:ethyl acetate = 5:1, R_f(**32a**)= 0.40) yielded 176 mg (32%) **32a** as a white solid and 94 mg (17%) **22a** as a colorless oil.
Following general procedure D [MeLi (5.40 ml of a 1.6 M solution in hexane, 8.6 mmol)], starting material **21** (501 mg, 3.4 mmol), gave, after work-up, 391 mg (71%, 94% pure according to cap. GC) **32a** as a white solid.
32a: m.p.: 43-47 °C (*n*-pentane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.15-6.11 (m, 2H, H_8 and H_9), 5.70 A of AB (dd, $J_{4,5}$=5.6 Hz, $J_{4,6}$=1.5 Hz, 1H, H_4), 5.62 B of AB (dd, $J_{5,6}$=2.1 Hz, 1H, H_5), 2.87 (bs, 1H, H_1), 2.67 A of AB (bd, $J_{2,6}$=6.6 Hz, 1H, H_6), 2.59 (bs, 1H, H_7), 1.91 B of AB (d, 1H, H_2), 1.70 (bs, 1H, -OH), 1.46 A of AB (d, $J_{10a,10s}$=8.6 Hz, 1H, H_{10s}), 1.36 (s, 3H, $-CH_3$), 1.31 B of AB (dt, $J_{2,10a}$≈$J_{6,10a}$≈1.5 Hz, 1H, H_{10a}). IR (CCl_4): υ 3605 (free -OH), 3640-3100 (H-bonded -OH), 3045 (C-H, unsat.), 3020-2780 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 162 (4,M^+), 145 (49,-OH), 144 (96,-H_2O), 129 (89,-H_2O,-CH_3), 96 (83,-C_5H_6), 81 (20,-C_5H_6,-CH_3), 66 (100,$C_5H_6^+$). EI/HRMS *m/e*: 162.1050 (calc. for $C_{11}H_{14}O$ (M^+): 162.1045).

exo-3-*n-Butyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **32b**
Following general procedure D [*n*-BuLi (1.00 ml of a 1.6 M solution in hexane, 1.6 mmol)], starting material **21** (131 mg, 0.90 mmol), gave, after work-up, 159 mg of a yellow oil. Flash chromatography (hexane:ethyl

acetate = 4:1, R_f(**32b**)= 0.57) yielded 98 mg (53%) **32b** as a colorless oil.
32b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.16-6.11 (m, 2H, H_8 and H_9), 5.67 (bs, 2H, H_4 and H_5), 2.82 (bs, 1H, H_1 or H_7), 2.61 A of AB (d, $J_{2,6}$=6.8 Hz, 1H, H_6), 2.59 (bs, 1H, H_1 or H_7), 1.93 B of AB (d, 1H, H_2), 1.63-1.56 (m, 4H, -$CH_2CH_2CH_2CH_3$), 1.47 (bd, $J_{10a,10s}$=8.7 Hz, 1H, H_{10a} or H_{10s}), 1.33-1.29 (m, 4H, -$CH_2CH_2CH_2CH_3$, -OH and H_{10a} or H_{10s}), 0.91-0.88 (m, 3H, -$CH_2CH_2CH_2CH_3$). IR (CCl_4): υ 3610 (free -OH), 3650-3080 (H-bonded -OH), 3040 (C-H, unsat.), 3020-2800 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 204 (20,M^+), 187 (86,-OH), 147 (29,-*n*-Bu), 144 (28,-C_3H_7,-OH), 138 (11,-C_5H_6), 129 (39,-*n*-Bu,-H_2O), 120 (21,-C_5H_6,-H_2O), 95 (100,-C_5H_6,-C_3H_7), 82 (27,-C_5H_5,-*n*-Bu), 66 (38,$C_5H_6^+$), 57 (7,*n*-Bu^+), 43 (4,$C_3H_7^+$). EI/HRMS *m/e*: 204.1510 (calc. for $C_{14}H_{20}O$ (M^+): 204.1514).

exo-3-*sec-Butyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **32c**
Following general procedure D [*n*-BuLi (3.50 ml of a 1.4 M solution in hexane, 4.9 mmol)], starting material **21** (367 mg, 2.5 mmol), gave, after work-up, 568 mg of a brown oil. Flash chromatography (hexane:ethyl acetate = 3:1, R_f(**32c**)= 0.82) yielded 258 mg (52%) of an approximately 1:1 mixture of two diastereomers of **32c** as a colorless oil.
32c (two diastereomers, ratio ≈ 1:1 according to 400 MHz ^{1}H-NMR): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.17-6.12 (m, 2H, H_8 and H_9), 5.72 resp. 5.71 A of AB (dd, $J_{4,5}$=5.7 Hz, $J_{4,6}$ resp. $J_{5,6}$=2.0 Hz, 1H, H_4 or H_5), 5.67-5.63 B of AB (m, 1H, H_4 or H_5), 2.77 (bs, 1H, H_1 or H_7), 2.59 (bs, 1H, H_1 or H_7), 2.55 A of AB (bd, $J_{2,6}$=6.9 Hz, 1H, H_6), 1.96 B of AB (d, 1H, H_2), 1.73-1.60 (m, 1H, -$CH(CH_3)CH_2CH_3$), 1.52-1.40 (m, 2H, -OH and H_{10a} or H_{10s}), 1.32 B of AB (bd, $J_{10a,10s}$=8.7 Hz, 1H, H_{10a} or H_{10s}), 1.05-0.86 (m, 8H, -$CH(CH_3)CH_2CH_3$). IR (CCl_4): υ 3600 (free -OH), 3680-3100 (H-bonded -OH), 3040-3020 (C-H, unsat.), 3020-2780 (C-H, sat.) cm^{-1}. EI/MS: *m/e* (%) 204 (8,M^+), 187 (7,-OH), 186 (14,-H_2O), 175 (1,-C_2H_5), 157 (23,-C_2H_5,-H_2O), 147 (56,-*s*-Bu), 139 (20,-C_5H_5), 129 (22,-*s*-Bu,-H_2O), 120 (15,-C_5H_6,-H_2O), 109 (100,-C_5H_6,-C_2H_5), 91 (19,-C_5H_6,-C_2H_5,-H_2O), 81 (30,-C_5H_6,-*s*-Bu), 66 (58,$C_5H_6^+$), 57 (19,*s*-Bu^+). EI/HRMS *m/e* : 204.1519 (calc. for $C_{14}H_{20}O$ (M^+): 204.1514).

exo-3-*Phenyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*dien*-endo-3-*ol* **32d**
Following general procedure D [PheLi (1.70 ml of a 2.0 M solution in hexane, 3.4 mmol)], starting material **21** (269 mg, 1.8 mmol), gave, after work-up, 466 mg of a brown oil. Flash chromatography (hexane:ethyl acetate = 8:1, R_f(**32d**)= 0.51) yielded 310 mg (78%) **32d** as a white solid.
32d: m.p.: 57-58 °C (*n*-pentane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H, H_{ortho}), 7.34-7.30 (m, 2H, H_{meta}), 7.23-7.19 (m, 1H, H_{para}), 6.15 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), 6.10 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 5.90 A of AB (dd, $J_{4,5}$=5.5 Hz, $J_{4,6}$ resp. $J_{5,6}$=2.1 Hz, 1H, H_4 or H_5), 5.79 B of AB (dd, $J_{4,6}$ resp. $J_{5,6}$=1.5 Hz, 1H, H_4 or H_5), 3.02 (bs, 1H, H_1 or H_7), 2.83 A of AB (bd, $J_{2,6}$=6.8 Hz, 1H, H_6), 2.69 (bs, 1H, H_1 or H_7), 2.24 B of AB (d, 1H, H_2), 1.94 (s, 1H, -0H), 1.64 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10s}), 1.42 B of AB (dt, $J_{2,10a}$≈$J_{6,10a}$≈1.5 Hz, 1H, H_{10a}). IR (CCl_4): υ 3600 (free -OH), 3650-3100 (H-bonded -OH), 3055 (C-H, unsat.), 3010-2800 (C-H, sat.), 700 (phenyl, mono-subst.) cm^{-1}. EI/MS: *m/e* (%) 224 (3,M^+), 207 (100,-OH), 158 (35,-C_5H_6), 147 (4,-C_6H_5), 142 (35,-C_5H_5,-OH), 129 (12,-C_6H_5,-H_2O), 77 (7,$C_6H_5^+$), 66 (4,$C_5H_6^+$). EI/HRMS *m/e*: 224.1200 (calc. for $C_{16}H_{16}O$ (M^+): 224.1201).

exo-9-*Bromo*-6-*methyl*-7-*oxatetracyclo*[6.3.0.$0^{2,6}$.$0^{3,10}$]*undec*-4-*ene* **34a**
Following general procedure E [NBS (142 mg, 0.80 mmol)], starting material **30a** (98 mg, 0.60 mmol), gave, after work-up, 131 mg (90%) **34a**. An analytical sample was obtained by flash chromatography (hexane:ethyl acetate = 10:1, R_f(**34a**)= 0.52).
34a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.85 A of AB (d, $J_{4,5}$=5.6 Hz, 1H, H_5), 5.64 B of AB (ddd, $J_{3,4}$=2.8 Hz, $J_{?,4}$=0.7 Hz, 1H, H_4), 4.63 (d, $J_{1,8}$=5.0 Hz, 1H, H_8), 4.13 (d, $J_{9,10}$=2.1 Hz, 1H, H_9), 3.08 A of AB (bdt, $J_{3,10}$≈$J_{3,4}$, $J_{2,3}$=8.5 Hz, 1H, H_3), 2.79 (bt, $J_{1,2}$=5.3 Hz, 1H, H_1), 2.65 B of AB (dd, 1H, H_2), 2.43 (bs, 1H, H_{10}), 2.42 A of AB (bd, $J_{11a,11s}$=11.0 Hz, 1H, H_{11a}), 1.92 B of AB (bd, 1H, H_{11s}), 1.33 (s, 3H, -CH_3). IR (CCl_4): υ 3050 (C-H, unsat.), 3020-2820 (C-H, sat.), 1040 (C-O) cm^{-1}. EI/MS: *m/e* (%) 242/240 (23/24,M^+), 213/211 (16/17,-HCO), 161 (100,-Br), 133/131 (29/30,$C_4H_4Br^+$), 121 (78,-CBr,-CO), 93/91 (42/46,CBr^+), 80 (100,$C_5H_4O^+$), 66 (9,$C_5H_6^+$). EI/HRMS *m/e*: 242.0130 (calc. for $C_{11}H_{13}OBr$ (M^+,^{81}Br): 242.0129).

exo-9-*Bromo*-6-*n-butyl*-7-*oxatetracyclo*[6.3.0.$0^{2,6}$.$0^{3,10}$]*undec*-4-*ene* **34b**
Following general procedure E [NBS (107 mg, 0.60 mmol)], starting material **30b** (56 mg, 0.27 mmol), gave, after work-up, 68 mg (89%) **34b**. An analytical sample was obtained by flash chromatography (hexane:ethyl acetate = 10:1, R_f(**34b**)= 0.45).
34b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.87 A of AB (d, $J_{4,5}$=5.6 Hz, 1H, H_5), 5.65 B of AB (dd, $J_{3,4}$=2.6 Hz, 1H, H_4), 4.64 (d, $J_{1,8}$=4.7 Hz, 1H, H_8), 4.13 (d, $J_{9,10}$=2.1 Hz, 1H, H_9), 3.06 A of AB (bdt, $J_{3,10}$≈$J_{3,4}$, $J_{2,3}$=8.5 Hz, 1H, H_3), 2.73-2.68 (m, 2H, H_1 and H_2), 2.43 (bs, 1H, H_{10}), 2.41 A of AB (d, $J_{11a,11s}$=10.9 Hz, 1H, H_{11a}), 1.92 (bd, 1H, H_{11s}), 1.62-1.57 (m, 2H, -$CH_2CH_2CH_2CH_3$), 1.35-1.23 (m, 4H, -$CH_2CH_2CH_2CH_3$), 0.90 (t, $J_{CH2,CH3}$=6.8 Hz, 3H, -$CH_2CH_2CH_2CH_3$). IR (CCl_4): υ 3050 (C-H, unsat.), 3020-2820 (C-H, sat.), 1040 (C-O) cm^{-1}. EI/MS: *m/e* (%) 284/282 (7/7,M^+), 255/253 (9/9,-HCO), 242/240 (12/12,-C_3H_6), 203 (38,-Br),

175 (8,-Br,-CO), 163 (26,-CBr,-CO), 122 (70,-Br,-C_5H_5O), 80 (100,$C_5H_4O^+$), 66 (9,$C_5H_6^+$), 57 (10,*n*-Bu^+), 29 (9,HCO^+). EI/HRMS *m/e*: 282.0622 (calc. for $C_{14}H_{19}OBr$ (M^+,^{79}Br): 282.0619).

exo-9-*Bromo*-6-*sec-butyl*-7-*oxatetracyclo*[6.3.0.$0^{2,6}$.$0^{3,10}$]*undec*-4-*ene* **34c**
Following general procedure E [NBS (196 mg, 1.1 mmol)], starting material **30c** (mixture of two diastereomers, 65 mg, 0.32 mmol), gave, after work-up, 88 mg (97%) **34c** as a mixture of two diastereomers. An analytical sample was obtained by flash chromatography (hexane:ethyl acetate = 10:1, R_f(**34c**)= 0.48).
34c (two diastereomers, ratio ≈ 1:1 according to 400 MHz ^{1}H-NMR): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.90 resp. 5.89 A of AB (d, $J_{4,5}$=5.7 Hz, 1H, H_5), 5.66-5.63 B of AB (m, 1H, H_4), 4.65 (d, $J_{1,8}$=4.8 Hz, 1H, H_8), 4.14 (d, $J_{9,10}$=2.2 Hz, 1H, H_9), 3.08-3.04 (m, 1H, H_3), 2.74 (dd, $J_{2,3}$=5.3 Hz, $J_{1,2}$=2.8 Hz, 1H, H_2) resp. 2.72 (dd, $J_{2,3}$=5.0 Hz, $J_{1,2}$=2.6 Hz, 1H, H_2), 2.67 (bs, 1H, H_1), 2.43 (bs, 1H, H_{10}), 2.41 A of AB (d, $J_{11a,11s}$=10.1 Hz, 1H, H_{11a}), 1.92 B of AB (bd, 1H, H_{11s}), 1.59-1.52 and 0.95-0.83 (2m, 2H and 7H, -$CH(CH_3)CH_2CH_3$). IR (CCl_4): υ 3050 (C-H, unsat.), 3020-2780 (C-H, sat.), 1040 (C-O) cm^{-1}. EI/MS: *m/e* (%) 284/282 (12/12,M^+), 255/253 (5/5,-HCO), 203 (32,-Br), 175 (5,-Br,-CO), 163 (15,-CBr,-CO), 122 (100,-Br,-C_5H_5O), 66 (17,$C_5H_6^+$), 57 (17,*s*-Bu^+), 29 (15,HCO^+). EI/HRMS *m/e*: 282.0619 (calc. for $C_{14}H_{19}OBr$ (M^+,^{79}Br): 282.0619).

exo-9-*Bromo*-6-*phenyl*-7-*oxatetracyclo*[6.3.0.$0^{2,6}$.$0^{3,10}$]*undec*-4-*ene* **34d**
Following general procedure E [NBS (92 mg, 0.52 mmol)], starting material **30d** (94 mg, 0.42 mmol), gave, after work-up, 120 mg (95%) **34d**. An analytical sample was obtained by crystallization from *n*-hexane.
34d: m.p.: 69-70 °C (*n*-hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 4H, $H_{arom.}$), 7.26-7.23 (m, 1H, $H_{arom.}$), 6.03 A of AB (d, $J_{4,5}$=5.6 Hz, 1H, H_5), 5.87 B of AB (dd, $J_{3,4}$=2.8 Hz, 1H, H_4), 4.90 (d, $J_{1,8}$=5.0 Hz, 1H, H_8), 4.28 (d, $J_{9,10}$=2.1 Hz, 1H, H_9), 3.24 A of AB (bdt, $J_{3,10}$≈$J_{3,4}$, $J_{2,3}$=8.7 Hz, 1H, H_3), 2.95 B of AB (dd, $J_{1,2}$=5.2 Hz, 1H, H_2), 2.84 (bt, 1H, H_1), 2.53 (bs, 1H, H_{10}), 2.49 A of AB (d, $J_{11a,11s}$=10.9 Hz, 1H, H_{11a}), 1.96 B of AB (bd, 1H, H_{11s}). IR (CCl_4): υ 3060-3020 (C-H, unsat.), 3010-2840 (C-H, sat.), 1250 (C-O), 1040 (C-O), 860 (C-O), 715 and 700 (phenyl, mono-subst.) cm^{-1}. EI/MS: *m/e* (%) 304/302 (35/32,M^+), 275/273 (7/7,-HCO), 223 (51,-Br), 195 (15,-Br,-CO), 183 (22,-CBr,-CO), 155 (24,-CBr,-CO,-C_2H_4), 142 (100,-Br,-C_5H_5O), 77 (8,$C_6H_5^+$), 66 (2,$C_5H_6^+$). EI/HRMS *m/e*: 304.0287 (calc. for $C_{16}H_{15}OBr$ (M^+,^{81}Br): 304.0286).

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12. 1,4-Addition of the *sec*-butyl group, which was attempted at temperatures ranging from -78 to 0 °C, was unsuccessful due to the thermal instability of the *s*-Bu_2CuLi reagent. Also a number of alternatives, *viz.* *s*-BuMgBr/CuCl with or without BF_3-etherate[5b,13], *s*-$Bu_2Cu(CN)Li_2$[14], *s*-Bu_3ZnLi[15] and the use of pure Me_2S.CuBr complex as a source of uncontaminated Cu^{1+} failed to yield significant amounts of desired products.
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16. 5-Methyl-*endo*- and *exo*-tricyclodecadienone **24** and **25** were obtained by intramolecular aldol condensation of *endo,endo*-2,3-diacetylbicyclo[2.2.1]hepta-5-ene. In a forthcoming publication we will elaborate on this approach to 4-substituted and 5-substituted *endo*- and *exo*-tricyclodecadienones.
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19. Structures were minimized, using the Allinger force field method (MM2-M in MODEL).
20. H_{4n} refers to the *endo*-proton at C_4 and H_{4x} to the corresponding *exo*-proton. A detailed analysis of the ^{1}H-NMR spectra of 1,4-adducts (**13a-c**, **14a**, **19a-c**, **20a-c**, **22a-c** and **23a**) by means of selective decoupling and NOE experiments revealed a long range coupling between H_2 (H_6 in **19a-c** and **20a-c**) and H_{4x}, which is not present between H_2 (H_6 in **19a-c** and **20a-c**) and H_{4n}. This feature makes it possible to distinguish between the absorptions due to H_{4n} and H_{4x} in the ^{1}H-NMR spectra of the 1,4-adducts.
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27. We recently discovered, that the C_8-C_9 double bond in *exo*-4,5-epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one is also spontaneously epoxidized by molecular oxygen during synthesis and crystallization.
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