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PHOTOCHEMISTRY OF SUBSTITUTED 1-(BUT-3-ENYL)-INDANES[1]

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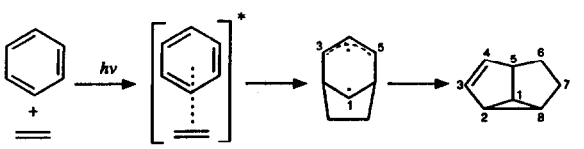
Summary - The intramolecular arene-olefin photocycloaddition was studied with 1-substituted indanes. The chemo- as well as the regioselectivity is primarily controlled by donor substituents in the indane moiety. Selected transformations of the photoproducts are described.

Introduction.

The discovery of the intermolecular meta-photoreaction of benzene with olefinic double bonds by Wilzbach and Kaplan,[2] Bryce-Smith and Gilbert[3] and its intramolecular variety by Morrison,[4] which leads via meta-addition to tri- and tetracyclic products, has found synthetic applications and induced mechanistic studies.[5] Particularly P. Wender has shown, that by judicious choice of substituents in the aromatic ring tetracyclic intermediates are obtained which are readily transformed into natural products like α-cedrene, isocomene, modhephene, hirsutene, coriolin,[6a] silphinene,[6b] silphiperfol-6-ene,[6c] rudmollin,[6d] and more recently laurenene[6e] and subergorgic acid and retigeranic acid.[6f]

Mechanistic studies, which are based on product studies and spectroscopic investigations, inter alia by Bryce-Smith,[7] Cornelisse,[8] Scharf[9] and Mattay[11] have led to a rather detailed mechanistic model, which may serve as a rationale for design of further experiments. The mode of addition (substitution, ortho- resp. meta-cycloaddition) has been correlated with the difference in ionization potentials of the arene and the olefin.[7] The probability of meta-cycloaddition increases with the decreasing difference of the ionization potentials. More recently it has been proposed that the ortho- vs. meta- mode of addition, to be described by the Rehm-Weller equation[10] is controlled by the free enthalpies of photoinduced electron transfer between the arene and the olefin. Substitution is favored with $\Delta G<0$ whereas ortho- vs. meta-cycloaddition decreases with $\Delta G>0$. Based on the observation of an exciplex the meta-cycloaddition is initiated by the formation of an exciplex between the electronically excited benzene moiety and the olefin, which leads via a [2+3] cycloaddition to a diradical which forms via bond formation between C(1) and C(3) resp. C(5) tricyclic structures containing a bicyclo[3.3.0]octane and vinylcyclopropane substructure (Scheme 1).



Scheme 1

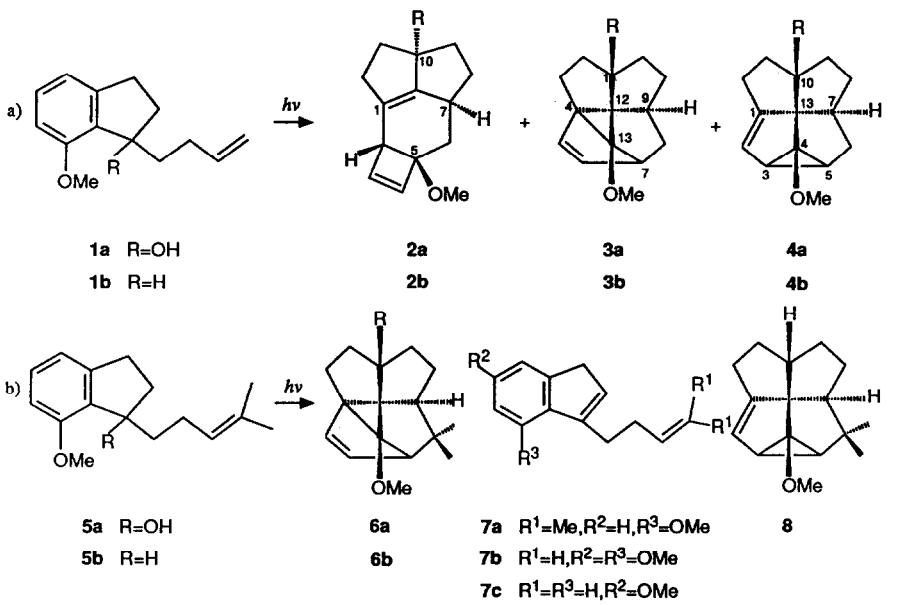
The regioselectivity in the [2+3] cycloaddition step is controlled by substituents at the aromatic ring and steric interactions induced by cis-alkyl groups at the terminal C of the olefin.[11]

Electron-donating substituents like methoxy and alkyl are consistently found at C(1) in the product, whereas electron-withdrawing substituents like cyano and trifluoro-methyl are preferentially placed at C(3) and C(5) (cf. Scheme 1). The effect of solvent polarity, albeit small, is compatible with the formation of an intermediate with some dipolar character. Hitherto addition of a protic solvent to the proposed dipolar diradical has not been observed.

We have used the photoinduced intramolecular meta-cycloaddition for the synthesis of 'architectonic' molecules like fenestranes[13] and report here results, which we obtained in the attempt to prepare [5.5.5.5]fenestranes like **4a,b** directly by photoreaction of 1-(but-3-enyl)-indanes (Scheme 2).

Results.

We have reported, that the photo-induced reaction of the substituted 7-methoxyindane **1a** in t-butylmethyl ether led to the photoproducts **2a**, **3a** and **4a** in the ratio of 4-5:3-4:1 with a total yield of 45%.[12] The unexpected formation of **2a**, which is initiated by a [2+2] rather than a [2+3] cycloaddition as the major product led to the question, whether this is due to the interaction between the methoxy group and the second substituent in the benzylic position.



1a R=OH **1b** R=H

2a **2b**

3a **3b**

4a **4b**

5a R=OH **5b** R=H

6a **6b**

7a R^1=Me,R^2=H,R^3=OMe **7b** R^1=H,R^2=R^3=OMe **7c** R^1=R^3=H,R^2=OMe

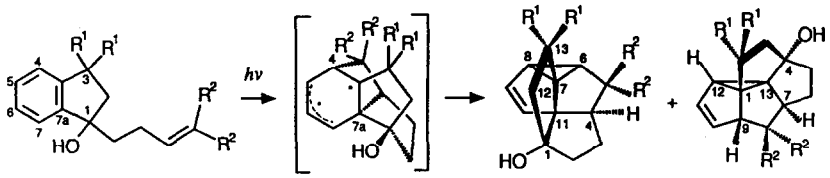
8

Scheme 2

When **1b** was irradiated in the same solvent, the products **2b**, **3b** and **4b** were obtained in an average ratio of 3.5-1.5-1 with a total yield of 47%. It thus appears that the formation of **2** is only slightly affected by the substituent pattern in the 1-position of the indanes of **1a** and **1b**.

Model considerations suggested, that the meta photoaddition could be enhanced at the expense of the ortho-cycloaddition, which eventually led to **2a,b**, by introduction of methyl groups at the terminal C-atom of the double bond. Indeed, when **5a** was irradiated, **6a** was obtained, albeit in small yield, as the exclusive product arising from an initial meta-cycloaddition. The major photoreaction which competed in this case with the [2+3] cycloaddition gave via photodehydration the indene derivative **7a** in high yield. Similarly, when **5b** was irradiated, only photoproducts arising from meta-cycloaddition, viz. **6b** and **8** were observed, again in small yield.

The photoreactions of **1a,b** and **5a,b** clearly show, that the methoxy group at 7-position controls the mode of addition. It was to be expected, that in absence of this substituent the electron-donating properties of the cyclopentane ring would become apparent.
Indeed, when **9a** is photolysed, the tetracyclic products **11a** and **12a** are formed in a ratio of 1:2 with a total yield of 65% (Scheme 3). The structure of **11a** and **12a** established by advanced NMR methodology (cf. Table 1,2), clearly suggest that these photoproducts are formed via **10** by an initial [2+3] cycloaddition between the double bond and C(4) and C(7a) rather than C(6) and C(7a).



9a R^1=R^2=H	**10**	**11a** 23%	**12a** 43%
9b R^1=H, R^2=Me		**11b** 24%	**12b** 28%
9c R^1=Me, R^2=H		**11c** 12%	**12c** 30%

Scheme 3

In the same manner **9b** with two methyl groups at the terminal C-atom of the double bond gives upon irradiation the tetracyclic products **11b** and **12b** in a ratio of 1:1.2 with a total yield of 52%.
In contrast to expectation, the photoreaction of **9c**, which contains two methyl groups in 3-position, leads via addition of the double bond to C(4) and C(7a) to **11c** and **12c** in a ratio of 1:2.5 with a total yield of 42%. Apparently the interaction between the methyl group in 3-position located cis to the butenyl side chain in position 1 is too small to shift the meta-cycloaddition from C(7a) and C(4) to C(7a) and C(6).

Structure elucidation of the photoproducts.

The structure of **2b-4b**, **6a**, **8**, **11a-c** and **12a-c** was established by 1D- and 2D- NMR spectroscopy.
Major spectroscopic features of the structure of **2b** were comparable to those of **2a**.[12] Apart from C(1)-C(13) and C(5)-C(6), all ^{13}C-^{13}C connectivities of the ring skeleton were established by INADEQUATE measurements (cf. exp. part). ^1H-^1H COSY measurements supported the adjacency of C(2)H-C(3)H-C(4)H and $C(6)H_2$-C(7)H-$C(8)H_2$-$C(9)H_2$-C(10)H-$C(11)H_2$-$C(12)H_2$. The cis- relationship of the protons at C(7) and C(10), located trans to the methoxy group at C(4) was established by NOE measurements.
Comparison of the NMR spectra of **3b** and **4b** with those of **3a** and **4a**[12] as well as the analysis of homo- and hetero-COSY results lead to the structure of **3b** and **4b**.
The structure proposed for compounds **6a**, **6b** resp. **8** is based on detailed analyses of NMR spectra and their comparison with those of **3a**, **3b** resp. **4b**. In **6a** a three-carbon fragment [C(5)H=C(6)H-C(7)H] separated from a C(9)H-$C(10)H_2$-$C(11)H_2$- and an isolated $C(12)H_2$-$C(13)H_2$ substructure could be detected. Further evidence for the structure of **6a** was provided by C-H and ^1H-^1H-connectivities.
Similarly, in the NMR spectra of **8**, a C(2)H-C(3)H-C(5)H substructure, separated from a C(7)H-$C(8)H_2$-$C(9)H_2$-C(10)H-$C(11)H_2$-$C(12)H_2$ fragment could be detected.
Analysis of the homo- and hetero-COSY results of compound **11a** indicated the presence of an isolated $C(12)H_2$-$C(13)H_2$ fragment and a separate $C(2)H_2$-$C(3)H_2$-C(4)H-C(5)H_2-C(6)H substructure with C(6)H being part of the remaining vinyl-cyclopropyl unit.

Similarly, the structure of **11b,c** was established (cf. Table 1). For **11b** the presence of isolated $C(2)H_2$-$C(3)H_2$-C(4)H and $C(12)H_2$-$C(13)H_2$ fragments and a C(6)H-C(8)H subunit connected to a double bond were apparent. NOE results indicated the proximity of the α-Me group at C(5) to C(4)H and to both olefinic protons and of the vinylic proton at C(10) to C(4)H.

Table 1. NMR data of **11a,b,c**

	11a			**11b**			**11c**		
Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)OH	86.680(s)	broad	-	87.116(s)	broad	-	87.201(s)	1.67(broad)	-
$C(2)H_2$	43.563(t)	1.91-2.01(m,1H) 2.11-2.19(m,1H)	$C(3)H_2$	42.966(t)	1.76-1.85(m,1H) 2.05-2.09(m,1H)	$C(3)H_2$	44.871(t)	1.70-1.82(m,1H) 1.98(dd,1H)	$C(3)H_2$
$C(3)H_2$	29.443(t)	1.61-1.69(m,2H)	$C(2)H_2C(4)H$	26.837(t)	1.54-1.62(m,1H) 1.67-1.77(m,1H)	$C(2)H_2C(4)H$	28.997(t)	1.41-1.58(m,2H)	$C(2)H_2C(4)H$
C(4)H	56.902(d)	2.25-2.32(m)	$C(3)H_2C(5)H_2$	66.715(d)	2.05-2.09(m)	$C(3)H_2$	57.889(d)	2.13-2.21(m)	$C(3)H_2C(5)H_2$
$C(5)H_2$	31.877(t)	1.77(ddd,1H) 1.83-1.90(m,1H)	C(4)H,C(6)H	46.233(s)	-	-	31.800(t)	1.70-1.82(m,2H)	C(4)H,C(6)H
C(6)H	32.529(d)	1.57-1.62(m)	$C(5)H_2$	46.694(d)	1.37(d)	C(8)H	36.289(d)	1.70-1.82(m)	$C(5)H_2C(8)H$
C(7)	57.248(s)	-	-	59.069(s)	-	-	66.921(s)	-	-
C(8)H	39.115(d)	1.82-1.89(m)		37.989(d)	1.70-1.75(m)	C(6)H	33.696(d)	1.58-1.62(m)	C(6)H,C(9)H
C(9)H	130.188(d)	5.73(dd)		131.410(d)	5.83(dd)		128.640(d)	5.59(dd)	C(8)H,C(10)H
C(10)H	130.046(d)	5.51(d)		133.236(d)	5.47(d)		132.631(d)	5.53(d)	C(9)H
C(11)	81.155(s)	-	-	82.329(s)	-	-	83.089(s)	-	-
$C(12)H_2$	46.704(t)	2.09-2.17(m,1H) 2.24-2.32(m,1H)	$C(13)H_2$	45.938(t)	2.02-2.12(m,1H) 2.20-2.26(m,1H)	$C(13)H_2$	62.301(t)	2.07-2.18(m,2H)	-
$C(13)H_2$	27.633(t)	1.80-1.88(m,1H) 2.06-2.14(m,1H)	$C(12)H_2$	28.425(t)	1.91-1.97(m,1H) 2.01-2.08(m,1H)	$C(12)H_2$	36.289(s)	-	-
α-Me	-	-	-	28.459(q)	1.07(s,3H)	-	29.718(q)	0.98(s,3H)	-
β-Me	-	-	-	28.738(q)	0.99(s,3H)	-	26.528(q)	0.94(s,3H)	-

a) multiplicity determined by DEPT; b) assigned according to hetero-COSY measurements; c) approximate multiplicity; d) COSY results.

For compound **11c**, an isolated $C(12)H_2$- group and a $C(2)H_2$-$C(3)H_2$-C(4)H-$C(5)H_2$-C(6)H-C(8)H-C(9)H-C(10)H substructure were detected. Further structural information was obtained from NOE results: upon irradiation of the α-Me group at C(13), C(8)H (and $C(12)H_2$) showed a signal enhancement, whereas irradiation of the β-Me group affected C(6)H.

The structure of **12a-c**, which like **11a-c** contains each a triquinacane substructure has been established by detailed analysis of their NMR spectra as well (Table 2).

Table 2. NMR data of **12a,b,c**

	12a			**12b**			**12c**		
Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	55.579(s)	-	-	56.537(s)	-	-	63.834(s)	-	-
$C(2)H_2$	26.717(t)	1.82-1.90(m,1H) 2.04-2.13(m,1H)	$C(3)H_2$	29.551(t)	2.03-2.18(m,2H)	$C(3)H_2$	39.281(s)	-	-
$C(3)H_2$	38.628(t)	1.42-1.52(m,1H) 2.01-2.10(m,1H)	$C(2)H_2$	39.610(t)	1.44-1.52(m,1H) 2.03-2.18(m,1H)	$C(2)H_2$	55.455(t)	1.49(d,α-H) 2.02(d,β-H)	β-C(3)H α-C(3)H
C(4)OH	88.023(s)	1.68(broad)	-	88.410(s)	broad	-	87.246(s)	1.40-1.48(broad)	-
$C(5)H_2$	37.816(t)	1.80-1.89(m,2H)	$C(6)H_2$	40.342(t)	1.84-1.89(m,2H)	$C(6)H_2$	41.006(t)	1.88-1.94(m,1H) 2.06-2.12(m,1H)	$C(6)H_2$
$C(6)H_2$	29.948(t)	1.40-1.49(m,1H) 2.10-2.21(m,1H)	$C(5)H_2C(7)H$	26.078(t)	1.65-1.71(m,1H) 1.99-2.09(m,1H)	$C(5)H_2C(7)H$	29.771(t)	1.40-1.46(m,1H) 2.06-2.12(m,1H)	$C(5)H_2C(7)H$
C(7)H	38.184(d)	2.31(dd)	$C(6)H_2C(8)H_2$	48.629(d)	1.99-2.03(m)	$C(6)H_2$	38.238(d)	2.18-2.25(m)	$C(6)H_2C(8)H_2$
$C(8)H_2$	50.336(t)	1.98-2.06(m,2H)	C(7)H,C(9)H	62.325(s)	-	-	52.279(t)	1.89-1.99(m,2H)	C(7)H,C(9)H
C(9)H	52.223(d)	2.89-2.91(m)	$C(8)H_2C(10)H$	62.993(d)	2.57(d)		49.962(d)	2.95-2.99(m)	$C(8)H_2C(10)H$
C(10)H	128.766(d)	5.52(ddd)	C(9)H,C(11)H	128.901(d)	5.59(ddd)		128.689(d)	5.42(ddd)	C(9)H,C(11)H
C(11)H	134.918(d)	5.76(dd)	C(10)H,C(12)H	134.531(d)	5.81(dd)		134.752(d)	5.67(dd)	C(10)H,C(12)H
C(12)H	38.398(d)	2.45-2.74(m)	C(11)H	37.159(d)	2.24(m)		38.178(d)	2.35-2.37(m)	C(11)H
C(13)	59.816(s)	-	-	63.702(s)	-	-	64.161(s)	-	-
α-Me	-	-	-	26.785(q)	0.83(s,3H)	-	29.398(q)	0.97(s,3H)	-
β-Me	-	-	-	24.014(q)	1.07(s,3H)	-	24.649(q)	1.18(s,3H)	-

a) multiplicity determined by DEPT; b) assigned according to hetero-COSY measurements; c) approximate multiplicity; d) COSY results.

Compound **12a** contains an isolated ethylidene bridge [$C(2)H_2$-$C(3)H_2$] and a separate $C(5)H_2$-$C(6)H_2$-C(7)H-$C(8)H_2$-C(9)H subunit, which is bonded via C(5) to the quaternary C(4)OH and via C(9) to the vinylcyclopropyl group.

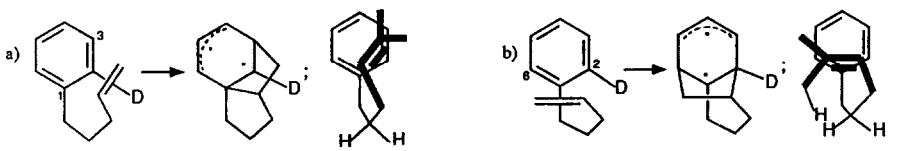
Analysis of NMR spectra of compound **12b** revealed the presence of an ethylidene fragment [$C(2)H_2$-$C(3)H_2$] and a $C(5)H_2$-$C(6)H_2$-C(7)H subunit, which are each flanked by quaternary C-

atoms. Additional NOE experiments showed, that the C(5)-Me group at δ=1.07 ppm is cis to C(7)H and close to C(10)H.

For compound **12c**, the presence of a $C(5)H_2$-$C(6)H_2$-C(7)H-$C(8)H_2$-C(9)H substructure flanked by a vinylcyclopropane and a quaternary C(4)OH group could be established. Based on NOE results, the C(2)-Me group at δ=0.97 ppm is located syn to the H at C(12) and cis to the C(3)H at δ=1.49 ppm, which also leads to a signal enhancement of C(12)H.

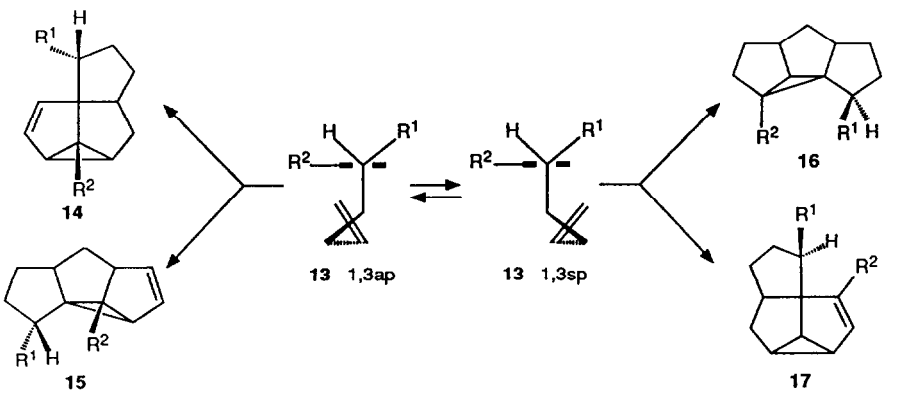
Discussion.

The intramolecular photoinduced arene-olefin cycloaddition is discussed in terms of the general mechanistic features established for the intermolecular case. Discussion of the meta- vs. ortho-cycloaddition depends on the knowledge of the the ionization potentials (IP's) of the arene and the olefin and further terms for the Rehm-Weller equation. The 1,3- vs. 2,6-regioselectivity of the meta-cycloaddition may be discussed in terms of electronic stabilization and steric interactions provided by substituents.



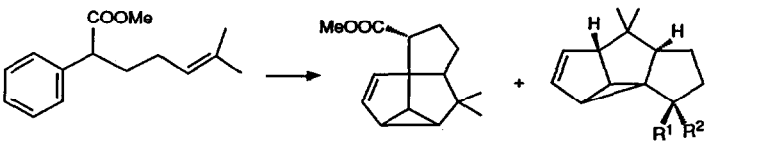
Scheme 4

For example, in the intramolecular photoreaction of substituted 5-phenylpentenes, 1,3-addition occurs preferentially, if not exclusively, with either a MeO- or a Me- group in the ortho-position of the phenyl ring (Scheme 4, D=OMe or Me). This preference is due to the stabilizing interaction excerted by the donor MeO- substituent in the formation of the intermediate (cf. Scheme 4a). 1,3-Addition is also enhanced over 2,6-addition in the presence of a (Z)-Me- group at the terminal C-atom of the double bond. The interaction between the (Z)-Me- group and the homoallylic CH_2- group destabilizes the conformation necessary for 2,6-addition (cf. Scheme 4b). In the presence of substituents in the benzylic, homoallylic or allylic position of 5-phenylpentene syn- and antiplanar conformations can be distinguished for the same diastereotopic side of the double bond in 1,3- and 2,6-cycloadditions. In principle, 5-phenylpentenes with benzylic substituents (Scheme 5, **13**, R^2=H) give rise to 'globular' (like **14** and **17**) and 'linear' (like **15** and **16**) cycloadducts (Scheme 5).[14]



Scheme 5

The formation of a 'globular' and the 'linear' photoproducts **19** resp. **20x,n**, the latter in an exo/endo ratio of 20:8, in the photoreaction of **18** is compatible with this scheme and points to subtle differences between the anti- and syn-planar conformations of **18** during cycloaddition (Scheme 6).[15]



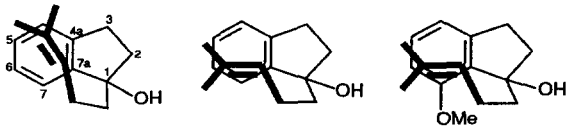
18 **19** **20** x R^1=H,R^2=COOMe
n R^1=COOMe,R^2=H

Scheme 6

Analogous mechanistic considerations may be applied to the photoinduced transformations of 1-(but-3-enyl)-indanes. Indeed, indane having an IP (8.46 eV[16]) similar to that of o-xylene (8.56 eV[17]), reacts upon irradiation intramolecularly with the double bond of the butenyl group exclusively in a 1,3- rather than a 2,6-mode (Scheme 3 and[18]). Ellis-Davies has interpreted the formation of products arising from the 1,3-mode in terms of the stabilization of the dipolar intermediate by the electron donating effect of the annulated cyclopentane.[18]

The 'globular' (**11a-c**) and 'linear' (**12a-c**) products obtained in the photoreaction of (**9a-c**) (Scheme 3) are formed via 1,3-cycloaddition and the syn-planar conformation (Scheme 7,a). Products of 1,5- or 2,6-mode with bond formation between the double bond and C(6)/C(7a) resp. C(7)/C(4a) have not been observed (Scheme 7, b).

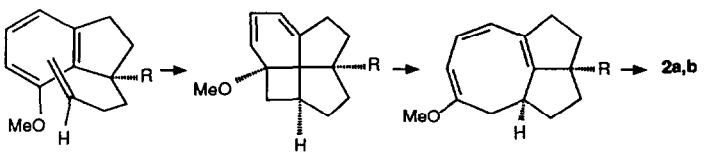
In the presence of a MeO group in 7-position of 1-(but-3-enyl)-indanes no products of meta-addition to C(7a) and C(4) could be detected in the photoreaction of **1a** and **1b**. Due to the strong regio-directing effect of the MeO group, only the 1,5-mode of meta-cycloaddition (Scheme 7,c), leading to bond formation between the double bond and C(6)/C(7a) was observed. The major photoproduct, however, formed in the case of **1a** and **1b** is due to ortho-addition (cf. Scheme 2).



a) 1,3sp b) 1,5ap c) 1,5

Scheme 7

We have proposed, that the unexpected formation of **2a** and **2b** proceeds via photoinduced [2+2] cycloaddition in such a way, that the highly strained cis,cis,trans,cis-[6.5.5.4]fenestrane **21a,b**, containing a trans-bicyclo[3.2.0]heptane subunit, is formed (Scheme 8). The latter undergoes a

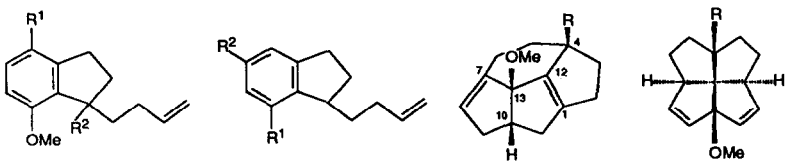


1a,b ('syn') **21a,b** **22a,b**

Scheme 8

6e⁻ suprafacial cycloreversion to give the triene **22a,b**, which during the irradiation leads via an allowed 4e⁻ sigmatropic ring closure to **2a** resp. **2b**. According to this mechanistic scheme, the cis-relationship between the substituents at C(7) and C(10) is established in the photoinduced formation of the ortho-cycloadduct **21a,b** and maintained during the subsequent pericyclic steps. This unique stereochemical feature of **2a** and **2b** is opposite to the trans-relationship of the substituents at C(1)/C(9) in **3a,b** and at C(7)/C(10) in **4a,b**, which is established during the photoinduced formation of the meta-cycloadduct as well (Scheme 1). It indicates, that the face selectivity of the double bond in this intramolecular meta-cycloaddition is opposite to that in the ortho-cycloaddition.

In order to explore the effect, which additional substituents might have on the photoreactions, the bichromophoric compounds **23a-c** and **24a-c** were prepared. Key steps of the synthesis of these compounds are the addition of but-3-enyl anions to the corresponding substituted indan-1-ones and Birch reduction. The MeO group in 4-position of **23a** could selectively be cleaved by treatment with Me_3SiI to give **23d**, from which **23b** and **23c** were readily obtained (cf. experimental part).



23a R^1=OMe,R^2=OH
23b R^1=OMe,R^2=H
23c R^1=OH,R^2=H
23d R^1=OAc,R^2=H
23e R^1=OSiMe$_3$,R^2=H
23f R^1=Me,R^2=H

24a R^1=R^2=OMe
24b R^1=OMe,R^2=OH
24c R^1=H,R^2=OMe

25a,b

26a,b

Scheme 9

When **23a** was irradiated in t-BME several products were formed, which decomposed during purification. Photoreaction of **23b** and **23c** lead only to polymeric material, a similar result[18] has been reported for **23e**. Irradiation of **24a** in t-BME gave 11% of **24b** and polymeric material, which also was observed in the photoreaction of **24c**.

Transformations of selected photoproducts.

It was early apparent, that the photoinduced meta-cycloaddition of butenyl indanes like **1a,b** might provide a short route to [5.5.5.5]fenestranes.[12] In view of this potential, it was of interest to investigate whether the photoproducts **2b** and **4b**, both being on the same energy hypersurface with [5.5.5.5]fenestranes, could be transformed into specifically functionalized fenestranes.

Thermolysis of **4b** in toluene in a sealed tube at 240°C leads to a single product **25b**, the structure of which was unambiguously established by NMR spectroscopy. As we had earlier observed, that **3a** as well **4a** gave only **25a** and not **26a**, it was not too surprising, that **26b** could not be detected in the thermolysis of **4b**, and that **3b** also gave **25b**. Even when **3b** and **4b** were each heated in C_6D_6 in a sealed NMR tube, no other product than **25b** could be detected.

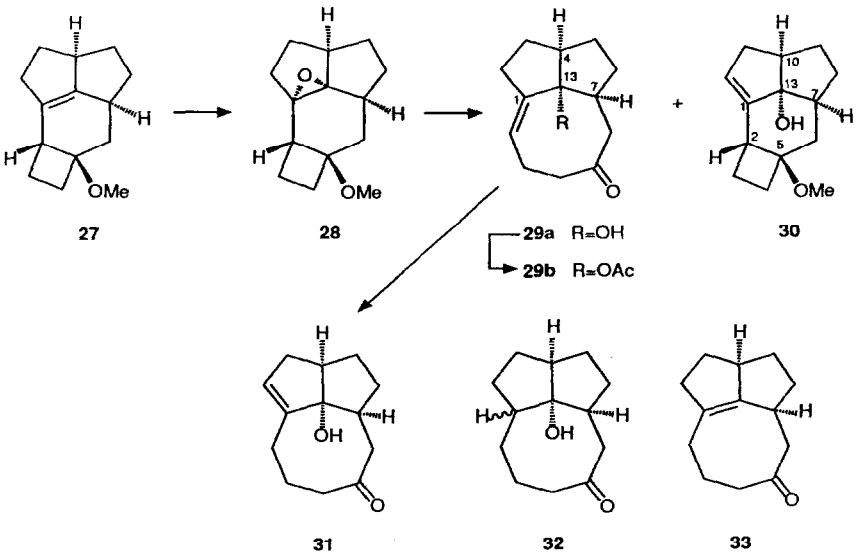
The fact, that a homodienyl [1,5]-sigmatropic H-shift in **4b** is not observed, might be due to steric constraints, which prevents the molecule of reaching a transition state with sufficient overlap between the orbitals involved. Instead, the 1,5-H shift occurs only after transformation of **4b** into **3b** via a vinyl-cyclopropyl rearrangement.[12]

Preliminary AM1 calculations for **3b** and **4b** indicate, that the distance between C(2) and the proton at C(10) is smaller in **3b** that in **4b** and that the deformation, necessary for the contact between C(2) and the H-C(10) bond requires more energy in **4b** than in **3b**.[19] The importance of carbon skeleton distortions for efficient transfer of hydrogen between distant C-atoms has been discussed by Menger.[20]

Inspection of the structural features of **2a,b** reveals that cleavage of the central bond of the cyclobutene substructure would give a functionalized cyclooctane, attached to a bicyclo[3.3.0]octane subunit in such a way, that a [5.5.5.5]fenestrane may be obtained by transannular C-C bond formation.

Whereas transannular reactions in eight-membered carbocycles are well known,[21] our experience with transannular carbene insertions in cyclooctanes appropriately substituted for direct generation of fenestranes has indicated that side reactions reduce the synthetic utility of this method.[22] The presence of a double bond at the bridgehead of the bicyclo[3.3.0]octane subunit of **2b** suggests, that a transannular C-C bond formation could be induced by carbenium ions. The fact, that H-C(7) and H-C(10) are cis to each other is of particular importance, because it suggests, that a cis,cis,cis,trans-[5.5.5.5]fenestrane*) would be obtained, if the transannular C-C bond formation could be realized with **2b**.

Hydrogenation of **2b** with Wilkinson's catalyst leads via selective reduction to **27** (Scheme 9). Treatment of compound **27** with m-CPBA leads to epoxidation from the exo side of the bicyclo[3.3.0]octene substructure and gave **28** as a single isomer. After refluxing of **28** in CH_3OH with CH_3COOH, the two allylic alcohols **29a** and **30** were obtained in a 7:1 ratio. Model considerations suggest, that the alignment of the C-O bond of the epoxide and the C-C bond of the cyclobutane subunit to be cleaved is such, that ring opening occurs via a stepwise mechanism rather than a concerted fragmentation.[24]



Scheme 10

The structure of **29a** and **30** was established by NMR spectroscopy. Analysis of the homo- and hetero- COSY results of **30** indicated the presence of a C(2)H-C(3)H_2-C(4)H_2 subunit and a

*) For a discussion of stereoisomerism in [m.n.o.p]fenestranes see ref.[23]

$C(6)H_2$-C(7)H-$C(8)H_2$-$C(9)H_2$-C(10)H-$C(11)H_2$-C(12)H substructure. The cis-relationship between C(7)H and C(10)H was obtained from NOE measurements: Irradiation of C(7)H leads to a signal enhancement of $C(8)H_{'exo'}$, which itself showed interaction with $C(9)H_{'exo'}$ as well as with $C(8)H_{'endo'}$. Irradiation of $C(9)H_{'exo'}$ leads to a signal enhancement of C(10)H and $C(9)H_{'endo'}$. Since **2b** was transformed into **30** without affecting the configuration of the bridgehead protons, this is further proof of the configuration of **2b**.

In order to introduce a double bond in **29** between C(1) and C(13) without affecting the cis-relationship of the bridgehead protons, reduction of the allylic alcohol with shift of the double bond was attempted. When **29a** was exposed to H_2 with Pd/C as catalyst for a short time, compound **31** together with a small amount of **32** was obtained. When the allylic acetate **29b** was treated with lithium triethylhydridoborate according to ref.[25] for a short time, only reduction of the carbonyl group was observed. The expected compound **33** could not be obtained even with a longer reaction time.

Concluding Remarks.

The photoinduced intramolecular meta-cycloaddition of substituted 1-(but-3-enyl)-indanes has been studied. Substituents do play an important role in the photocycloaddition and affect the outcome of the photolysis. A methoxy group at the 7-position of the indane derivatives excerts the expected directing effect, though the photoreaction occurs preferentially via a [2+2] and not via a [2+3] cycloaddition. The steric repulsion to be expected by the geminal dimethyl group is observed in **5a, 5b** but not in **9b, 9c**. Further work for transformation of **2b** into a cis, cis, cis, trans-[5.5.5.5]fenestrane are in progress.

EXPERIMENTAL

For general remarks see ref.[12] Abbreviations used: t-BME=tert.-butylmethyl ether, m-CPBA=meta-chloroperbenzoic acid. In the tables with NMR results the following footnotes and notations are used: a) multiplicity determined by DEPT; b) assigned according to hetero-COSY measurements; c) approximate multiplicity; d) COSY results; e) INADEQUATE results; f) decoupling results; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet; n=endo, x=exo. ^{1}H-NOE results are reported in the following way: C(X)-H irradiated (signal enhancement at C(Y)-H).

General procedure for irradiations: A solution of the 1-(but-3-enyl)-indanes in 350 ml t-BME was irradiated in a quartz vessel with a 500 W high pressure lamp (TQ 718, Hanau) for several hours. The yellow solution was filtered through silica gel, concentrated and submitted to medium-pressure chromatography with hexane-t-BME.

1-(But-3-enyl)-7-methoxyindane (1b). A solution of 6.55 g (30.0 mmol) 1-(but-3-enyl)-7-methoxyindan-1-ol[12] in 10 ml THF was added dropwise to a solution of 0.36 g (91.0 mmol) Li in a mixture of 100 ml NH_3 and 40 ml THF at -78°C during 30 min. After 30 min, NH_4Cl was added to discharge the blue color and the ammonia was allowed to evaporate. After work up, the crude material was purified by medium-pressure chromatography with hexane-t-BME=3:1. After recovery of 2.70 g starting material, 3.40 g (95%) **1b** was isolated as a colorless oil. Rf (hexane-t-BME=3:1): 0.80. IR: 3005m, 2940m, 1640w, 1590s, 1480s, 1260s, 1075s, 910m. ^{1}H-NMR: 1.30-2.40(stack, 6H), 2.80-

Table 3. NMR data of **2b**

Assignment	^{13}C-NMR[a] δ[ppm]	Adjacent[e] C-Atoms	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	133.391(s)	C(2),C(12)	-	-
C(2)H	47.602(d)	C(1),C(3),C(5)	3.28(broad)	C(3)H
C(3)H	141.040(d)	C(2),C(4)	6.23(dd)	C(2)H,C(4)H
C(4)H	135.987(d)	C(3),C(5)	6.19(dd)	C(3)H
C(5)	88.230(s)	C(2),C(4)	-	-
$C(6)H_2$	37.934(t)	C(7)	1.09(t,H_n) 2.10(m,H_x)	C(7)H
C(7)H	30.048(d)	C(6),C(8),C(13)	2.18(m)	$C(6)H_2$,C(8)H_2
$C(8)H_2$	34.624(t)	C(7),C(9)	1.72(dd,H_n) 2.13(m,H_x)	C(7)H,$C(9)H_2$
$C(9)H_2$	33.097(t)	C(8),C(10)	1.01(m,H_n) 1.89(dt,H_x)	$C(8)H_2$,C(10)H
C(10)H	50.079(d)	C(9),C(11),C(13)	2.94-3.03(m)	$C(9)H_n$,$C(11)H_2$
$C(11)H_2$	31.992(t)	C(10),C(12)	1.60(dddd,H_n) 2.22(dddd,H_x)	C(10)H,$C(12)H_2$
$C(12)H_2$	39.308(t)	C(1),C(11)	2.45(m,H_n) 2.86(dddd,H_x)	$C(11)H_2$
C(13)	153.774(s)	C(7),C(10)	-	-
OMe	51.653(q)	-	3.36(s,3H)	-

NOE results: C(2)-H [C(3)-H,C(12)-H_n,OMe]; C(3)-H [C(2)-H,C(4)-H]; C(4)-H [C(2)-H,C(3)-H,C(6)-H_n,C(7)-H,OMe]; C(6)-Hn [C(6)-H_xC(8)-H_n]; C(8)-H_n [C(6)-H_n,C(8)-H_x,C(9)-H_n]; C(8)-H_x [C(7)-H,C(8)-H_nC(9)H_x]; C(9)-H_n [C(8)-H_nC(9)-H_x,C(11)-H_n]; C(9)-H_x [C(8)-H_nC(9)-H_nC(10)-H]; C(10)-H [C(9)-H_xC(11)-H_x]; C(11)-H_n [C(9)-H_nC(11)-H_xC(12)-H_n]; C(12)-H_n [C(2)-H,C(11)-H_nC(12)-H_x]; C(12)-H_x [C(11)-H_n,C(12)-H_n]; OMe [C(2)-H,C(4)-H].

3.60(stack, 3H), 3.80(s, 3H), 4.90-5.30(stack, 2H), 5.60-6.30(m, 1H), 6.60-7.40(stack, 3H). MS: 202(10, M^+), 160(56), 147(100), 115(13), 91(16). Anal. calc. for $C_{14}H_{18}O$ (202.30): C 83.12, H 8.97; found: C 82.90, H 8.73.

Irradiation of 1b. A solution of 3.40 g (16.8 mmol) **1b** in t-BME was irradiated for 8 h. After work up, the yellow oil, which contained 17% of **1b** and **2b**, **3b** and **4b** in the ratio of 3.5:1.5:1 was separated by medium-pressure chromatography with hexane-t-BME=30:1 to give **2b** and **3b** in pure form. A pure sample of **4b** was obtained by an additional HPLC (DuPont column, 7 μm silica, 21.2 mm x 25 cm, hexane-t-BME=100:1):

5-Methoxytetracyclo[5.5.1.$0^{2,5}$.$0^{10,13}$]trideca-1(13),3-diene (2b). Yield: 1.00 g (31.5%, GC-purity ca. 95%). Rf (hexane-t-BME=30:1): 0.26. IR: 3005m, 2930s, 2860m, 1100m, 1080m, 1060m. NMR: see *Table 3*. MS: 202(52, M^+), 187(23), 173(50), 160(40), 147(100), 129(36), 115(37), 91(46). HR-MS: 202.1357 (calc. 202.1358).

13-Methoxypentacyclo[5.4.2.$0^{4,12}$.$0^{4,13}$.$0^{9,12}$]tridec-5-ene (3b). Yield: 0.26 g (11.4%, GC-purity ca. 95%). Rf (hexane-t-BME=30:1): 0.26. IR: 3010m, 2945s, 2855s, 1455m, 1405m, 1120s. NMR: see *Table 4*. MS: 202(4, M^+), 160(41), 148(12), 147(100), 131(11), 117(12), 115(14), 91(23). HR-MS: 202.1359 (calc. 202.1358).

4-Methoxypentacyclo[5.5.1.$0^{3,5}$.$0^{4,13}$.$0^{10,13}$]tridec-1-ene (4b). Yield: 0.14 g (4.3%, GC-purity ca. 92%). Rf (hexane-t-BME=30:1): 0.28. IR: 3005s, 2945s, 2860s, 1450s, 1370m, 1155m, 1105m, 1015m. NMR: see *Table 5*. MS: 202(3, M^+), 160(43), 148(12), 147(100), 131(10), 115(9), 91(17). HR-MS: 202.1357 (calc. 202.1358).

Table 4. NMR data of **3b**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)H	39.081(d)	2.46(m)	$C(2)H_x$,$C(11)H_2$
$C(2)H_2$	42.266(t)	1.71-1.77(m,H_n)	$C(1)H$,$C(2)H_n$,$C(3)H_2$
		1.99-2.05(m,H_x)	$C(1)H$,$C(2)H_n$,$C(3)H_n$
$C(3)H_2$	29.351(t)	1.94(m,H_n)	$C(2)H_x$,$C(3)H_x$
		2.24(dd,H_x)	$C(2)H_n$,$C(3)H_n$
C(4)	53.401(s)	-	-
C(5)H	132.133(d)	5.72(d)	C(6)H
C(6)H	127.258(d)	5.38(dd)	C(5)H,C(7)H
C(7)H	56.122(d)	3.40(m)	C(6)H,$C(8)H_2$
$C(8)H_2$	41.432(t)	1.65-1.69(m,2H)	C(7)H,C(9)H
C(9)H	40.834(d)	2.08-2.13(m)	$C(8)H_x$,$C(10)H_2$
$C(10)H_2$	37.855(t)	1.51-1.59(m,H_n)	$C(9)H$,$C(10)H_n$,$C(11)H_2$
		2.08-2.13(m,H_x)	$C(9)H$,$C(10)H_n$,$C(11)H_2$
$C(11)H_2$	37.855(t)	1.46-1.52(m,H_n)	$C(1)H$,$C(10)H_2$,$C(11)H_x$
		2.12-2.19(m,H_x)	$C(1)H$,$C(10)H_2$,$C(11)H_n$
C(12)	70.708(s)	-	-
C(13)	95.029(s)	-	-
OMe	56.453(q)	3.42(s,3H)	-

Table 5. NMR data of **4b**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	157.125(s)	-	-
C(2)H	109.052(d)	4.91(m)	$C(3)H^D$
C(3)H	39.460(d)	2.10(dd)	$C(2)H^D$,C(5)H
C(4)	92.860(s)	-	-
C(5)H	40.852(d)	2.15-2.21(m)	C(3)H,$C(6)H_2$
$C(6)H_2$	27.064(t)	1.77(dd,H_n)	C(5)H,$C(6)H_x$,C(7)H
		1.88(ddd,H_x)	C(5)H,$C(6)H_n$,C(7)H
C(7)H	58.605(d)	1.99(m)	$C(6)H_2$,$C(8)H_2$
$C(8)H_2$	33.295(t)	1.50-1.61(m,2H)	C(7)H,$C(9)H_2$
$C(9)H_2$	36.633(t)	1.24-1.34(m,H_n)	$C(8)H_2$,$C(9)H_x$,C(10)H
		2.15-2.21(m,H_x)	$C(8)H_2$,$C(9)H_n$,C(10)H
C(10)H	36.956(d)	2.60(m)	$C(9)H_2$,$C(11)H_2$
$C(11)H_2$	36.877(t)	1.63-1.67(m,H_n)	$C(10)H$,$C(11)H_x$,$C(12)H_2$
		2.15-2.21(m,H_x)	$C(10)H$,$C(11)H_n$,$C(12)H_2$
$C(12)H_2$	24.500(t)	2.13-2.24(m,2H)	$C(11)H_2$
C(13)	80.460(s)	-	-
OMe	56.614(q)	3.31(s,3H)	-

7-Methoxy-1-(4-methylpent-3-enyl)-indan-1-ol (5a). A solution of 4.7 g (29.0 mmol) 7-methoxyindan-1-one[14] in 30 ml THF was added to the Grignard reagent prepared from 0.80 g (33.0 mmol) Mg and 7.60 g (33.0 mmol) 5-iodo-2-methylpent-2-ene in 20 ml ether at 0°C. After 6 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-t-BME=1:1 to give 3.70 g (51%) of **5a** as a colorless oil. Rf (hexane-t-BME=1:1): 0.70. IR: 3560m, 2940m, 1600m, 1580m, 1480s, 1260s, 1080s. ^{1}H-NMR: 1.60(s, 3H), 1.65(s, 3H), 1.80-2.90(stack, 8H), 3.00(s, 1H), 3.90(s, 3H), 5.00-5.20(m, 1H), 6.60-7.40(stack, 3H). MS: 246(25, M^+), 228(30), 212(30), 174(46), 164(80), 163(100), 160(100), 157(55), 145(22).

Irradiation of 5a. A solution of 1.40 g (5.70 mmol) **5a** in t-BME was irradiated for 8 h. After work up, the yellow oil was separated by medium-pressure chromatography with hexane-ether=9:1 (1% Et_3N added) to give 8 mg (0.5%) of **6a** and 0.60 g (46%) of **7a**. In another photoreaction, the yield of **7a** was lowered to 8.4% with an increase of polymeric material.

13-Methoxy-8,8-dimethylpentacyclo[5.4.2.$0^{4,12}$.$0^{4,13}$.$0^{9,12}$]tridec-5-en-1-ol (6a). Rf (hexane-t-BME=9:1, 1% Et_3N added): 0.10. IR: 3600-3500m, 2950s, 1750m, 1490m, 1450m, 1340s, 1120s. NMR: see *Table 6*. The NMR-spectrum contains 33% of an impurity. MS: 246(1, M^+), 228(2), 214(7), 163(100), 160(12), 148(8), 145(8), 131(4), 115(3), 83(4).

7-Methoxy-1-(4-methylpent-3-enyl)-ind-1-ene (7a). Rf (pentane-ether=9:1): 0.90. IR: 2950w, 1610w, 1480s,

Table 6. NMR data of **6a**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)OH	87.869(s)	broad	-
$C(2)H_2$	47.374(t)	1.90-2.15(m,1H)	$C(3)H_2$
		2.15-2.25(m,1H)	
$C(3)H_2$	27.477(t)	2.20-2.30(m,2H)	$C(2)H_2$
C(4)	53.590(s)	-	-
C(5)H	132.296(d)	5.80(d)	C(6)H
C(6)H	126.897(d)	5.45(dd)	C(5)H,C(7)H
C(7)H	67.087(d)	2.90(d)	C(6)H
C(8)	50.944(s)	-	-
C(9)H	49.939(d)	1.85-1.95(m)	$C(10)H_2$
$C(10)H_2$	44.424(t)	1.65-1.75(m,1H)	$C(9)H$,$C(11)H_2$
		2.05-2.15(m,1H)	
$C(11)H_2$	28.489(t)	1.60-1.80(m,2H)	$C(10)H_2$
C(12)	69.999(s)	-	-
C(13)	96.436(s)	-	-
OMe	57.108(q)	3.40(s,3H)	-
2xMe	23.583(q)	1.10(s,3H)	-
	24.167(q)	0.90(s,3H)	-

1320s, 1080s. ^{1}H-NMR: 1.60(s, 6H), 2.00-2.40(stack, 2H), 2.60-3.00(stack, 2H), 3.30(m, 2H), 3.80(s, 3H), 5.20(m, 1H), 6.10(m, 1H), 6.80-7.20(stack, 3H). MS: 228(15, M$^+$), 227(100), 214(15), 213(100), 185(25), 160(100), 159(100), 146(23), 143(38), 128(56). Anal. calc. for $C_{16}H_{20}O$ (228.18): C 84.16, H 8.83; found: C 83.89, H 8.70.

7-Methoxy-1-(4-methylpent-3-enyl)-indane (5b). A solution of 0.60 g (2.6 mmol) **7a** in 5 ml THF was added dropwise to a solution of 0.10 g (14.0 mmol) Li in a mixture of 50 ml NH_3 and 20 ml THF at -78°C. After 30 min, NH_4Cl was added to discharge the blue color and the ammonia was allowed to evaporate. After work up, the crude material was purified by medium-pressure chromatography with hexane-ether=9:1 to give 0.60 g (99%) of **5b** as a colorless oil. Rf (hexane-ether=9:1): 0.90. IR: 2950s, 1595s, 1480s, 1440m, 1260s, 1080s. ^{1}H-NMR: 1.40(m,1H), 1.61(s,3H), 1.69(s,3H), 1.80-1.93(stack,2H), 2.00-2.10(stack,2H), 2.20(m,1H), 2.80(m,1H), 2.97(m,1H), 3.30(m,1H), 3.81(s,3H), 5.17(m,1H), 6.68(d,1H), 6.83(d,1H), 7.12(t,1H). ^{13}C-NMR: 17.659(q), 25.725(q), 26.453(t), 30.506(t), 31.596(t), 33.623(t), 42.769(d), 55.040(q), 108.013(d), 116.925(d), 124.954(d), 127.654(d), 131.144(s), 135.026(s), 145.756(s), 156.426(s). MS: 230(32, M$^+$), 187(6), 173(44), 161(8), 160(100), 159(14), 147(97), 145(25), 131(33), 130(10), 117(15), 115(19), 91(27). Anal. calc. for $C_{16}H_{22}O$ (230.18): C 83.43, H 9.63; found: C 83.57, H 9.78.

Irradiation of 5b. A solution of 0.60 g (2.60 mmol) **5b** in t-BME was irradiated for 6h. After removing the solvent, the crude material was purified by medium-pressure chromatography with hexane-ether=9:1 to give 0.020 g (3.3%) of **6b** and 0.046 g (7.7%) of **8**.

13-Methoxy-8,8-dimethylpentacyclo[5.4.2.0^{4,12}.0^{4,13}.0^{9,12}]tridec-5-ene (6b). Rf (hexane-t-BME=9:1): 0.25. IR: 3100m, 2960s, 2880m, 1740w, 1640w, 1450m, 1380m, 1140m, 1100m. ^{1}H-NMR: 0.90(s, 3H), 1.00(s, 3H), 1.38(dd, 1H), 1.41-1.44(m, 1H), 1.69-1.76(stack, 2H), 1.81-1.91(stack, 2H), 1.98-2.05(m, 1H), 2.10-2.24(stack, 2H), 2.37-2.46(m, 1H), 2.88(d, 1H), 3.32(s, 3H), 5.42(dd, 1H), 5.81(d, 1H). ^{13}C-NMR: 23.938(q), 24.214(q), 29.093(t), 30.325(t), 37.944(t), 39.434(d), 42.263(t), 50.091(d), 50.281(s), 52.234(s), 56.676(d), 67.085(q), 70.317(s), 104.211(s), 125.789(d), 133.148(d). MS: 230(10, M$^+$), 172(30), 162(100), 147(98), 130(30), 116(20), 106(16), 90(30), 42(35). HR-MS: 230.1670 (calc. 230.1671).

Table 7. NMR data of **8**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	156.869(s)	-	-
C(2)H	111.773(d)	5.07-5.09(m)	C(3)H,C(5)H
C(3)H	53.571(d)	1.97-2.05(m)	C(2)H,C(5)H
C(4)	94.423(s)	-	-
C(5)H	39.354(d)	2.00-2.10(m)	C(3)H,C(5)H
C(6)	39.959(s)	-	-
C(7)H	56.661(d)	1.68-1.75(dd)	$C(8)H_2$
$C(8)H_2$	30.146(t)	1.50-1.65(m,2H)	$C(7)H,C(9)H_2$
$C(9)H_2$	35.783(t)	1.10-1.25(m,1H)	$C(8)H_2$,C(10)H
		2.12-2.22(m,1H)	
C(10)H	37.248(d)	2.59(q)	$C(9)H_2$,C(11)H_2
C(11)H_2	35.769(t)	1.60-1.67(m,1H)	C(10)H,C(12)H_2
		1.93-2.03(m,1H)	
C(12)H_2	24.517(t)	2.08-2.22(m,2H)	C(11)H_2
C(13)	80.167(s)	-	-
OMe	68.617(q)	3.32(s,3H)	-
2xMe	28.177(q)	1.06(s,3H)	-
	29.246(q)	1.08(s,3H)	-

4-Methoxy-6,6-dimethylpentacyclo[5.5.1.0^{3,5}.0^{4,13}.0^{10,13}]tridec-1-ene (8). Rf (hexane-t-BME=9:1): 0.30. IR: 3000w, 2950s, 2880m, 1470w, 1450m, 1380m, 1320w, 1160w, 1140m, 1080w, 1020w, 860w. NMR: see *Table 7*. MS: 230(5, M$^+$), 186(5), 172(33), 160(98), 146(100), 130(33), 116(28), 115(25), 90(50), 54(30), 31(30), 27(45), 17(25). HR-MS: 230.1670 (calc. 230.1671).

1-(But-3-enyl)-indan-1-ol (9a). A solution of 2.64 g (20.0 mmol) indan-1-one in 15 ml THF was added at 0°C to the Grignard reagent prepared from 0.85 g (35.0 mmol) Mg and 4.05 g (30.0 mmol) 4-bromobut-1-ene in 30 ml THF. After 2 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-ether=7:5 (0.05% Et_3N added). After recovery of 0.47 g starting material, 2.00 g (65%) of **9a** was obtained as a colorless oil. Rf (hexane-ether=7:5): 0.31. IR: 3600m, 3010s, 2950s, 1645m, 1480m, 1460m, 915s. ^{1}H-NMR: 1.75-2.40(stack, 7H), 2.75-3.15(stack, 2H), 4.84-5.30(stack, 2H), 5.60-6.30(m, 1H), 7.20-7.55(m, 4H). MS: 133(100,M$^+$-55), 115(6), 91(10), 77(9), 55(14), 28(14), 18(18). Anal. calc. for $C_{13}H_{16}O$ (188.27): C 82.94, H 8.57; found: C 82.88, H 8.29.

Irradiation of 9a. A solution of 2.00 g (10.6 mmol) **9a** in t-BME was irradiated for 2.5 h. After work up, the yellow oil was separated by medium-pressure chromatography with hexane-t-BME=1:1 (0.05% Et_3N added):

Pentacyclo[5.4.2.0^{4,11}.0^{6,8}.0^{7,11}]tridec-9-en-1-ol (11a). Yield: 0.45 g (23%). Rf (hexane-ether=7:5): 0.28. IR: 3600w, 3010m, 2950s, 2870m, 1315m. NMR: see *Table 1*. MS: 188(2, M$^+$), 170(1), 133(100), 116(8), 91(7), 55(3). Anal. calc. for $C_{13}H_{16}O$ (188.27): C 82.94, H 8.57; found: C 83.15, H 8.31.

Pentacyclo[5.5.1.0^{1,9}.0^{4,13}.0^{12,13}]tridec-10-en-4-ol (12a). Yield: 0.85 g (43%). Rf (hexane-ether=7:5): 0.22. IR: 3610m, 3450w, 3060w, 3010s, 2950s, 2870s, 1350m, 1090m, 995s, 975s.

NMR: see *Table 2*. MS: 133(100, M^+-55), 115(11), 91(16), 77(9), 55(9), 28(14), 18(8). Anal. calc. for $C_{13}H_{16}O$ (188.27): C 82.94, H 8.57; found: C 82.97, H 8.73.

1-(4-Methylpent-3-enyl)-indan-1-ol (9b). A solution of 6.60 g (50.0 mmol) indan-1-one in 20 ml THF was added at 0°C to the Grignard reagent prepared from 2.42 g (100.0 mmol) Mg and 16.3 g (100.0 mmol) 5-bromo-2-methylpent-2-ene in 60 ml THF. After 2 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-ether=7:5 to give 5.90 g (55%) of **9b** as a yellowish oil. Rf (hexane-ether=7:5): 0.42. IR: 3600m, 3520w, 3010s, 2970s, 2930s, 2855m, 1480m, 1460m. ^{1}H-NMR: 1.60(s, 3H), 1.70(s, 3H), 1.80-2.40(stack, 7H), 2.73-3.15(stack, 2H), 5.00-5.40(m, 1H), 7.20-7.60(stack, 4H). MS: 216(4, M^+), 198(10), 183(8), 144(16), 133(100), 130(55), 115(8), 91(8), 69(9), 55(7), 41(15). Anal. calc. for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.18, H 9.28.

Irradiation of 9b. A solution of 1.86 g (8.61 mmol) **9b** in t-BME was irradiated for 2 h. The solvent was removed and the residue purified by medium-pressure chromatography with hexane-t-BME=2:1:

5,5-Dimethylpentacyclo[5.4.2.0^{4,11}.0^{6,8}.0^{7,11}]tridec-9-en-1-ol (11b). Yield: 0.44 g (24%). Rf (hexane-t-BME=3:1): 0.24. IR: 3600m, 3460w, 3010s, 2955s, 2870s, 1470m, 1450m. NMR: see *Table 1*. MS: 216(5, M^+), 183(11), 147(83), 133(100), 115(19), 91(27), 77(14). HR-MS: 216.1515 (calc. 216.1514).

8,8-Dimethylpentacyclo[5.5.1.0^{1,9}.0^{4,13}.0^{12,13}]tridec-10-en-4-ol (12b). Yield: 0.52 g (28%). Rf (hexane-t-BME=3:1): 0.15. IR: 3610m, 3450w, 3010s, 2960s, 2870s, 1470m, 960s. NMR: see *Table 2*. MS: 216(4, M^+), 183(14), 147(58), 133(100), 115(13), 91(21), 77(10). Anal. calc. for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.02, H 9.30.

1-(But-3-enyl)-3,3-dimethylindan-1-ol (9c). A solution of 2.40 g (15.0 mmol) 3,3-dimethylindan-1-one[26] in 20 ml THF was added at 0°C to the Grignard reagent prepared from 0.60 g (25.0 mmol) Mg and 3.0 g (22.0 mmol) 4-bromobut-3-ene in 20 ml THF. After 1.5 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-t-BME=9:1. After recovery of 0.62 g starting material, 1.65 g (69%) of **9c** was isolated as a colorless oil. Rf (hexane-t-BME=4:1): 0.59. IR: 3600m, 3460w, 3015s, 2960s, 2940s, 2865m, 1645m, 1480m, 1455m, 1365. ^{1}H-NMR: 1.33(s, 3H), 1.40(s, 3H), 1.76(s, 1H), 1.90-2.50(stack, 6H), 4.90-5.40(stack, 2H), 5.70-6.30(m, 1H), 7.30-7.60(stack, 4H). MS: 216(2, M^+), 198(4), 183(3), 161(100), 143(22), 128(15). Anal. calc. for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.22, H 9.35.

Irradiation of 9c. A solution of 0.50 g (2.3 mmol) **9c** in t-BME was irradiated for 3.5 h. After removing of the solvent, the residue was purified by medium-pressure chromatography with hexane-t-BME=3:1 to yield starting material (0.086 g) and **11c** and **12c**:

13,13-Dimethylpentacyclo[5.4.2.0^{4,11}.0^{6,8}.0^{7,11}]tridec-9-en-1-ol (11c). Yield: 0.050 g (12%, obtained after preparative GC separation, GC-purity ca. 98%). Rf (hexane-t-BME=3:1): 0.28. IR: 3610w, 3010m, 2960s, 2870m. NMR: see *Table 1*. MS: 216(3, M^+), 161(100), 143(23), 128(17), 115(12), 91(12). Anal. calc. for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.37, H 9.13.

2,2-Dimethylpentacyclo[5.5.1.0^{1,9}.0^{4,13}.0^{12,13}]tridec-10-en-4-ol (12c). Yield: 0.13 g (30%, GC-purity ca. 95%). Rf (hexane-t-BME=3:1): 0.19. IR: 3610m, 3450w, 3010s, 2960s, 2940s, 2870m, 1455m, 1365m. NMR: see *Table 2*. MS: 216(5, M^+), 201(4), 198(2), 183(3), 161(100), 143(12), 128(7), 91(6). Anal. calc. for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.68, H 9.48.

1-(But-3-enyl)-4,7-dimethoxyindan-1-ol (23a). A solution of 0.80 g (4.17 mmol) 4,7-dimethoxyindan-1-one[27] in 20 ml THF was added at 0°C to the Grignard reagent prepared from 0.15 g (6.0 mmol) Mg and 0.81 g (6.0 mmol) 4-bromo-but-1-ene in 7 ml THF. After 0.5 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-ether=1:1 (0.5% Et_3N added) to give 0.72 g (70%) **23a** as a colorless oil. Rf (hexane-ether=1:1): 0.42. IR: 3575w, 3010m, 2945m, 2840m, 1495s, 1465m, 1440m, 1255s, 1080m, 915w. ^{1}H-NMR: 1.77-2.47(stack, 6H), 2.67-3.07(stack, 2H), 3.15(s, 1H), 3.80 (s, 6H), 4.83-5.25(stack, 2H), 5.60-6.20(m, 1H), 6.70(s, 2H). MS: 248(M^+, 10), 230(16), 193(100), 178(27), 163(10), 115(7). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.65, H 7.93.

1-(But-3-enyl)-4,7-dimethoxyindane (23b). A solution of 6.20 g (25.0 mmol) **23a** in 10 ml THF was added dropwise to a solution of 0.555 g (80.0 mmol) Li in a mixture of 100 ml NH_3 and 40 ml THF at -78°C during 30 min. After 30 min, NH_4Cl was added to discharge the blue color and the ammonia was allowed to evaporate. After work up, the crude material was purified by medium-pressure chromatography with hexane-ether=9:1 to give 4.07 g (72%) **23b**

as a colorless oil. Rf (hexane-ether=9:1): 0.53. IR: 3010m, 2940m, 2840m, 1640w, 1494s, 1465m, 1440m, 1255s, 1090m, 1075m, 915m. ^{1}H-NMR: 1.43-2.43(stack, 6H), 2.70-3.10(stack, 2H), 3.10-3.60(m, 1H), 3.80(s, 6H), 4.85-5.30(stack, 2H), 5.60-6.30(m, 1H), 6.66 (s, 2H). MS: 232(M^+, 60), 190(44), 177(100). Anal. calc. for $C_{15}H_{20}O_2$ (232.32): C 77.55, H 8.68; found: C 77.75, H 8.78.

1-(But-3-enyl)-4-hydroxy-7-methoxyindane (23c). A solution of 1.60 g (8.0 mmol) trimethylsilyl iodide and 1.53 g (6.6 mmol) **23b** in 20 ml CH_2Cl_2 was refluxed for 2 days. After work up, the crude compound **23e** 2.0 g was added to a mixture of 4.70 g (15.0 mmol) tetrabutylammonium fluoride in 50 ml THF. After 1 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with CH_2Cl_2 to give 0.74 g (52%) **23c** as white crystals. Rf (CH_2Cl_2): 0.69. IR: 3605m, 3450w, 3010m, 2945m, 2840m, 1640w, 1495s, 1260s, 1080s, 1000m, 915m. ^{1}H-NMR: 1.30-2.50(stack, 6H), 2.70-3.10(stack, 2H), 3.10-3.60(m, 1H), 3.80(s, 3H), 4.87-5.40(stack, 3H), 5.63-6.35(m, 1H), 6.63 (s, 2H). MS: 218(M^+, 27), 176(47), 163(100), 147(15), 107(17), 91(12), 77(10), 28(16). Anal. calc. for $C_{14}H_{18}O_2$ (218.30): C 77.03, H 8.31, found: C 76.86, H 8.32.

4-Acetoxy-1-(but-3-enyl)-7-methoxyindane (23d). A solution of 1.30 g (6.0 mmol) **40c** and 1.60 g (20.0 mmol) CH_3COCl in 20 ml $CHCl_3$ and 5 ml pyridine was stirred at 0°C for 30 min. After filtration through Celite and silica gel and removal of the solvent, the crude material was purified by flash chromatography with hexane to give 1.20 g (77%) **23d** as a yellowish oil. Rf (hexane-ether=5:1): 0.58. IR: 3010w, 2940m, 2840w, 1755s, 1490s, 1370m, 1180s, 1080m, 1025m, 915m. ^{1}H-NMR: 1.40-2.25(stack, 6H), 2.27(s, 3H), 2.60-3.10(stack, 2H), 3.10-3.60(m, 1H), 3.80(s, 3H), 4.87-5.30(stack, 2H), 5.60-6.30(m, 1H), 6.60-7.05(dd, 2H). MS: 260(M^+, 21), 218(60), 176(63), 163(100). Anal. calc. for $C_{16}H_{20}O_3$ (260.33): C 73.82, H 7.74; found: C 73.28, H 7.99.

1-(But-3-enyl)-5,7-dimethoxyind-1-ene (7b). A solution of 2.90 g (15.1 mmol) 5,7-dimethoxyindan-1-one[27] in 30 ml THF was added at 0°C to the Grignard reagent prepared from 0.50 g (20.0 mmol) Mg and 2.70 g (20.0 mmol) 4-bromo-but-1-ene in 20 ml THF. After 2 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-ether=7:5 (0.05% Et_3N added) to give 2.00 g (55%) **7b** as a white solid. Rf (hexane-ether=7:5): 0.69. IR: 3010m, 2940m, 2840w, 1605s, 1465m, 1320m, 1155s, 1090m. ^{1}H- NMR: 2.15-3.10(stack, 5H), 3.20-3.40(m, 1H), 3.80(s, 6H), 4.85-5.35(stack, 2H), 5.65-6.30(stack, 2H), 6.30-6.80(stack, 2H). MS: 230(M^+, 100), 215(30), 189(96), 175(75), 159(34), 145(30), 115(24). Anal. calc. for $C_{15}H_{18}O_2$ (230.31): C 78.23, H 7.88; found: C 78.02, H 7.74.

1-(But-3-enyl)-5-methoxyind-1-ene (7c). A solution of 5.00 g (31.0 mmol) 5-methoxyindan-1-one in 50 ml THF was added at 0°C to the Grignard reagent prepared from 0.97 g (40.0 mmol) Mg and 4.86 g (36.0 mmol) 4-bromo-but-1-ene in 30 ml THF. After 1 h at r.t. and work up, the crude material was purified by medium-pressure chromatography with hexane-ether=7:5 (0.05% Et_3N added). After recovery of 1.00 g starting material, 3.10 g (61%) **7c** was obtained as a yellowish oil. Rf (hexane-ether=7:5): 0.32. IR: 3010m, 2940m, 2915m, 2840w, 1610s, 1480s, 1285m, 1255s, 1240s, 1140m, 1030m, 915m. ^{1}H-NMR: 2.35-3.10(stack, 4H), 3.23-3.47(stack, 2H), 3.83(s, 3H), 4.90-5.37(stack, 2H), 5.67-6.40(stack, 2H), 6.80-7.50(stack, 3H). MS: 200(M^+, 65), 185(18), 159(100), 144(39), 128(28), 115(38). Anal. calc. for $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; found: C 83.51, H 8.17.

1-(But-3-enyl)-5,7-dimethoxyindane (24a). A solution of 2.60 g (11.3 mmol) **7b** in 10 ml THF was added dropwise to a solution of 0.245 g (35.0 mmol) Li in a mixture of 50 ml NH_3 and 20 ml THF at -78°C. After 1 h, NH_4Cl was added to discharge the blue color and the ammonia was allowed to evaporate. After work up, the crude material was purified by medium-pressure chromatography with hexane-t-BME=40:1 to give 1.45 g (55%) **24a** as a colorless oil. Rf (hexane-t-BME=40:1): 0.26. IR: 3010m, 2960m, 2940m, 2840m, 1605s, 1490s, 1465s, 1325m, 1145s, 1080m, 1045w, 915w. ^{1}H-NMR: 1.20-2.30(stack, 6H), 2.70-3.40(stack, 3H), 3.80(s, 6H), 4.87-5.30(stack, 2H), 5.60-6.20(m, 1H), 6.30- 6.55(stack, 2H). MS: 232(M^+, 14), 190(23), 177(100). Anal. calc. for $C_{15}H_{20}O_2$ (232.32): C 77.55, H 8.68; found: C 77.29, H 8.75.

1-(But-3-enyl)-5-hydroxy-7-methoxyindane (24b). A solution of 1.45 g (6.25 mmol) **24a** in t-BME was irradiated for 20 h. After removal of the solvent, the crude material was purified by medium-pressure chromatography with hexane-t-BME=4:1. After recovery of 0.10 g starting material, 0.15 g (11%) **24b** was obtained as a yellowish oil. Rf (hexane-t-BME=4:1): 0.22. IR: 3610m, 2950s, 1610s, 1340m, 1135s. ^{1}H-NMR: 1.40-2.40(stack, 6H), 2.60-2.93(stack, 2H), 3.05-3.50(stack, 2H), 3.70(s, 3H), 4.70-5.27(stack, 2H), 5.60-6.20(m, 1H), 6.23-6.77(stack, 2H).

1-(But-3-enyl)-5-methoxyindane (24c). A solution of 2.80 g (14.0 mmol) **7c** in 5 ml THF was added dropwise to a solution of 0.315 g (45.0 mmol) Li in a mixture of 50 ml NH_3 and 30 ml THF at -78°C during 20 min. After 30 min, NH_4Cl was added to discharge the blue color and the ammonia was allowed to evaporate. After work up, the crude material was filtered through a small silica gel column with hexane. After removal of solvent, 2.30 g (81%, GC-purity ca. 96%) **24c** was obtained as a colorless oil. Rf (hexane-ether=7:5): 0.78. IR: 3080w, 3005m, 2965s, 2930s, 2850m, 1640m, 1610m, 1590m, 1490s, 1255s, 1145m, 1035m, 915m. ^{1}H-NMR: 1.20-2.60(stack, 6H), 2.70-3.40(stack, 3H), 3.77(s, 3H), 4.85-5.30(stack, 2H), 5.60-6.30(m, 1H), 6.60-7.30(stack,3H). MS: 202(M^+, 9), 160(52), 147(100), 115(14), 91(19). Anal. calc. for $C_{14}H_{18}O$ (202.30): C 83.12, H 8.97; found: C 83.35, H 8.98.

13-Methoxytetracyclo[5.4.2.0^{4,12}.0^{10,13}]trideca-1(12),7-diene (25b). From 3b: A solution of 0.20 g (93% purity, 0.92 mmol) **3b** in 0.3 ml C_6D_6 was heated in a sealed NMR tube to 240° for 2 min. The crude product was purified by medium-pressure chromatography with hexane-t-BME=30:1 to give 0.16 g (86%, GC-purity ca. 99%) of **25b** as colorless oil. Rf (hexane-t-BME=30:1): 0.19. IR: 3010s, 2935s, 2850s, 1455m, 1440m, 1058s, 990m. NMR: see *Table 8*. MS: 202(21 M^+), 188(42), 187(24), 122(100), 91(21). Anal. calc. for $C_{14}H_{18}O$ (202.30): C 83.12, H 8.97; found: C 83.28, H 8.83.

From 4b: Similarly **25b** was obtained from 0.045 g (ca. 80% purity, 0.18 mmol) **4b** in a yield of 0.017 g (47%, GC-purity ca. 99%). According to IR, NMR, and its Rf value, it was identical with **25b** obtained from **3b**.

Table 8. NMR data of **25b**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	152.155(s)	-	-
C(2)H_2	29.791(t)	1.97-2.06(m,H_n) 2.24-2.30(m,H_x)	C(3)H_2
C(3)H_2	34.196(t)	1.82-1.90(m,H_n) 2.28-2.42(m,H_x)	C(2)H_2
C(4)H	37.654(d)	2.66(m)	C(5)H_2
C(5)H_2	36.129(t)	0.85(dddd,H_n) 1.86-1.92(m,H_x)	C(6)H_2
C(6)H_2	25.512(t)	2.14-2.24(m,2H)	C(5)H_2
C(7)	145.460(s)	-	-
C(8)H	122.085(d)	5.35(m)	
C(9)H_2	40.717(t)	1.96-2.04(m,H_n) 2.87(m,H_x)	C(10)H
C(10)H	45.692(d)	3.08(ddd)	C(9)H_2,C(11)H_2
C(11)H_2	39.061(t)	1.57(ddd,H_n) 2.93(m,H_x)	C(10)H
C(12)	148.565(s)	-	-
C(13)	97.449(s)	-	-
OMe	51.946(q)	3.24(s,3H)	-

NOE results: C(4)-H [C(3)-H_x,C(5)-H_x]; C(5)-H_x [C(5)-H_n C(6)-H_n]; C(8)-H [C(6)H_2,C(9)H_2]; C(9)-H_n [C(8)-H,C(9)-H_x,C(11)-H_n]; C(9)-H_x [C(8)-H,C(9)-H_n,C(10)-H]; C(10)-H [C(9)-H_x,C(11)-H_n,OMe]; C(11)-H_n [C(9)-H_n,C(11)-H_x]; C(11)-H_x [C(10)-H,C(11)-H_n]; OMe [C(10)-H].

5-Methoxytetracyclo[5.5.1.0^{2,5}.0^{10,13}]tridec-1(13)-ene (27). To a solution of 0.60 g (95% purity, 2.82 mmol) **2b** in 15 ml methanol was added 0.10 g (0.11 mmol) tris-[triphenylphosphin]-rhodium(I)-chloride. The mixture was treated with H_2 at r.t. for 160 min. After removing the solvent, the residue was filtered through a small silica gel column with ether. After removing the ether, the crude material was purified by medium-pressure chromatography with hexane-t-BME=20:1 to give 0.56 g (96%, GC-purity ca. 98%) **27** as a colorless oil. Rf (hexane-t-BME=9:1): 0.51. IR: 2990s, 2940s, 2860s, 1455m, 1330w. ^{1}H-NMR: 0.85(dd, 1H), 0.93-1.04(m, 1H), 1.43(m, 1H), 1.49-1.60(stack, 2H), 1.83-1.93(stack 3H), 1.99-2.22(stack, 3H), 2.25-2.44(stack, 3H), 2.50-2.55(m, 1H), 2.69-2.80(m, 1H), 2.88-2.97(m, 1H), 3.20(s, 3H). ^{13}C-NMR: 25.445(t), 25.625(t), 31.191(d), 32.004(t), 32.779(t), 34.166(t), 34.609(t), 38.603(t), 39.515(d), 48.879(d), 50.052(q), 85.206(s), 136.771(s), 149.290(s). MS: 204(M^+, 15), 175(27), 147(37), 131(46), 117(47), 105(40), 91(100). Anal. calc. for $C_{14}H_{20}O$ (204.31): C 82.30, H 9.87; found: C 82.51, H 9.96.

5-Methoxytetracyclo[5.5.1.0^{2,5}.0^{10,13}]tridec-1(12)-en-13-ol (29a) and tricyclo[5.5.1.0^{4,13}]tridec-1(12)-en-9-on-13-ol (30). To a mixture of 0.94 g (91% purity, 4.19 mmol) **27** and 1.0 g NaOAc in 10 ml CH_2Cl_2 was added dropwise a solution of 3.14 g (10.0 mmol) m-CPBA in 30 ml CH_2Cl_2 at 0°C. After 1 h at 0°C, the mixture was washed with sat. $Na_2S_2O_3$, Na_2CO_3 and NaCl solution and dried over anhydrous Na_2SO_4. After removing the solvent, the crude compound **28** 1.00g was dissolved in 40 ml methanol and 1 ml CH_3COOH and refluxed for 3.5 h. After removing the solvent, the residue was purified by medium-pressure chromatography with hexane-t-BME=1:2:

Tricyclo[5.5.1.0^{4,13}]tridec-1(12)-en-9-on-13-ol (29a). Yield: 0.54 g (63%). Rf (hexane-ether=7:5): 0.13. IR: 3600w, 3460w, 2955s, 1700s. ^{1}H-NMR: 1.21-1.27(m, 1H), 1.30-1.41(stack, 2H), 1.73-1.84(stack, 2H), 1.91-2.13(stack 4H), 2.23-2.36(stack, 5H), 2.62(ddd, 1H), 2.91(dd, 1H), 3.05-3.15(m, 1H), 5.72-5.77(m, 1H). ^{13}C-NMR: 22.529(t), 28.799(t), 30.390(t), 31.047(t), 35.519(t), 41.054(t), 46.093(t), 48.578(d), 54.020(d), 90.138(s), 124.319(d), 147.669(s), 213.209(s). MS: 206(M^+, 81), 188(68), 178(44), 165(62), 146(100), 118(79), 109(89), 91(57), 84(67). Anal. calc. for $C_{13}H_{18}O_2$ (206.28): C 75.69, H 8.80; found: C 75.42, H 8.88.

5-Methoxytetracyclo[5.5.1.0^{2,5}.0^{10,13}]tridec-1(12)-en-13-ol (30). Yield: 0.085 g (9%). Rf (hexane-ether=7:5): 0.26. IR: 3600m, 3440w, 3010s, 2950s, 1465m, 1090s, 1065s. NMR: see

Table 9. MS: 220(M^+, 32), 202(36), 192(100), 188(52), 173(31), 160(44), 146(54), 91(45), 85(58). Anal. calc. for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.11, H 9.23.

13-Acetoxytricyclo[5.5.1.0^{4,13}]tridec-1(12)-en-9-one (29b). A solution of 0.16 g (2.0 mmol) CH_3COCl and 0.206 g (1.0 mmol) **29a** in 10 ml $CHCl_3$ and 0.3 ml pyridine was refluxed for 3 h. After cooling and addition of CH_2Cl_2, the solution was washed 3x with sat. NaCl solution and dried over anhydrous Na_2SO_4. After removing the solvent, the crude material was purified by medium-pressure chromatography with hexane-ether=7:5 to give 0.17 g (65%) **29b** as a colorless oil. Rf (hexane-ether 7:5): 0.36. IR: 2960m, 1735s, 1705s, 1250s. ^{1}H-NMR: 1.24-1.36(stack, 2H), 1.39-1.45(m, 1H), 1.80-1.88(m, 1H), 1.90-1.96(m, 1H), 1.97(s,3H), 2.10-2.18(m, 1H), 2.20-2.35(stack, 2H), 2.38-2.47(stack, 4H), 2.49-2.59(stack, 2H), 2.60-2.68(m, 1H), 2.88-2.94(m, 1H), 5.72-5.78(m, 1H). ^{13}C-NMR: 21.530(q), 22.421(t), 30.701(t), 31.081(t), 32.210(t), 35.909(t), 43.131(t), 45.212(t), 47.307(d), 50.699(d), 97.741(s), 121.484(d), 144.311(s), 169.525(s), 212.442(s). MS: 248(M^+, 37), 206(100), 188(75), 146(38), 131(39), 117(46), 99(48), 91(37). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.44, H 8.34.

Table 9. NMR data of **30**

Assignment	^{13}C-NMR[a] δ[ppm]	^{1}H-NMR[b,c] δ[ppm]	^{1}H,^{1}H Connectivity[d]
C(1)	141.672(s)	-	-
C(2)H	40.870(d)	3.06-3.12(m)	$C(3)H_2$
$C(3)H_2$	28.805(t)	1.95-2.02(m,2H)	$C(2)H,C(4)H_2$
$C(4)H_2$	18.664(t)	1.87-1.95(m,2H)	$C(3)H_2$
C(5)	92.871(s)	-	-
$C(6)H_2$	30.519(t)	1.67(dd,H_n)	C(7)H
		1.87-1.95(m,H_x)	
C(7)H	43.775(d)	2.21-2.29(m)	$C(6)H_2,C(8)H_2$
$C(8)H_2$	30.813(t)	1.41-1.51(m,H_n)	$C(7)H,C(9)H_2$
		1.72-1.82(m,H_x)	
$C(9)H_2$	33.368(t)	1.15-1.23(m,H_n)	$C(8)H_2C(10)H$
		1.95-2.08(m,H_x)	
C(10)H	49.641(d)	2.26-2.33(m)	$C(9)H_2,C(11)H_x$
$C(11)H_2$	37.048(t)	1.84-1.91(m,H_n)	$C(11)H_x,C(12)H$
		2.67-2.75(m,H_x)	$C(10)H,C(11)H_n,C(12)H$
C(12)H	128.664(d)	5.57(m)	$C(11)H_2$
C(13)OH	79.442(s)	1.84-2.08(broad)	-
OMe	49.225(q)	3.17(s,3H)	-

NOE results: C(2)-H [C(12)-H]; C(6)-H_n [C(6)-H_x]; C(7)-H [C(8)-H_x]; C(8)-H_n [C(8)-H_x]; C(8)-H_x [C(7)-H,C(6)-H_nC(9)-H_x]; C(9)-H_n [C(6)-H_n,C(9)-H_x,C(10)-H]; C(9)-H_x [C(9)-H_n,C(10)-H]; C(10)-H [C(11)-H_x]; C(11)-H_n [C(9)-H_n]; C(12)-H [C(2)-H,C(11)H_2].

Tricyclo-[5.5.1.0^{4,13}]tridec-1-en-9-on-13-ol (31). A solution of 0.48 g (2.3 mmol) **29a** in 10 ml methanol was hydrogenated with 0.10 g Pd/C at r.t. for 30 min. After filtration through Celite and removal of the solvent, the residue was purified by medium-pressure chromatography with hexane-t-BME=1:2 to give 0.375 g (78%) **31** as a white solid. Another 0.048 g of C=C double bond reduced product was also obtained. Rf (hexane-t-BME=1:2): 0.29. IR: 3600m, 3470w, 2950s, 1695s, 1455m, 1035m. ^{1}H-NMR: 1.46-1.60(stack, 2H), 1.71-1.74(m, 1H), 1.77-1.89(stack, 2H), 1.93-2.02(m, 1H), 2.04-2.18(stack, 2H), 2.21-2.29(m, 1H), 2.31-2.43(stack, 4H), 2.47-2.61(stack, 4H), 5.51-5.56(m, 1H). ^{13}C-NMR: 25.741(t), 26.641(t), 29.747(t), 33.636(t), 37.883(t), 43.013(t), 43.212(t), 48.872(d), 54.411(d), 97.098(s), 132.433(d), 144.461(s), 214.921(s). MS: 206(M^+, 54), 188(54), 160(87), 147(51), 131(72), 118(86), 105(51), 95(91), 91(100). Anal. calc. for $C_{13}H_{18}O_2$ (206.28): C 75.69, H 8.80; found: C 75.78, H 8.77.

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