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Intramolecular *Meta* Photocycloaddition of Conformationally Restrained 5-Phenylpent-1-enes. Part I: Bichromophoric Cyclohexane Derivatives

Helma M. Barentsen, Edger G. Talman, Dennis P. Piet and Jan Cornelisse*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Abstract: The cis isomers of 1-allyl-2-phenylcyclohexane and 1-benzyl-2-vinylcyclohexane yield predominantly 1,3 addition, while the trans isomers show a high selectivity for 2,6 addition, which is explained by steric interactions. Introduction of a third substituent, OH or OCH_3, on the alkenyl substituted carbon of the cyclohexane ring gives almost exclusively 1,3 addition. This can mostly be explained in terms of more steric hindrance in the conformations leading to 2,6 addition.
From the results described it can be concluded that for 2,6 addition two conformations are available, while the energy difference between the 1,3 conformations is much larger and therefore a completely stereoselective 1,3 addition is found (except for **6**).

INTRODUCTION

The meta photocycloaddition of alkenes to arenes has been the subject of many investigations and has been reviewed recently[1,2]. The mechanism of the meta photocycloaddition, for the inter- as well as the intramolecular case, has been elucidated to a large extent. Much information has been obtained concerning the effects that substituents at the benzene ring and at the alkene moiety have on the course of the photoreaction. However, very few systematic investigations on the effects of substituents at the connecting chain on the intramolecular meta photocycloaddition have been performed. The inter-[3a] as well as the intramolecular[3b,c] variant have been used by Wender as a key step in the synthesis of complex molecules.

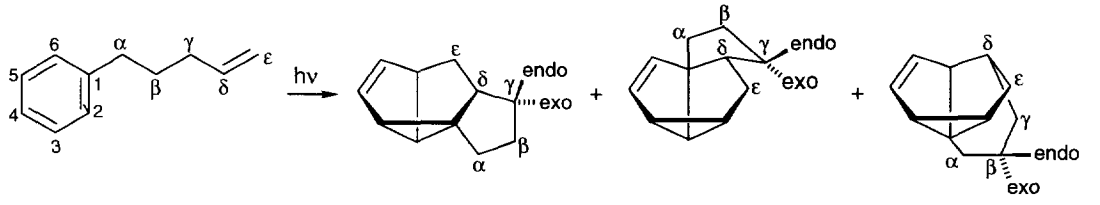


Figure 1 Intramolecular meta photocycloaddition of 5-phenylpent-1-ene. Endo/exo designation of substituents on the connecting chain in the adducts.

In practice only two modes of addition are possible (Figure 1): 2,6 and 1,3 addition, with one type of ring closure for 2,6 and two types of ring closure for 1,3 addition. Replacing the α, β or γ CH_2 units of the connecting chain in 5-phenylpent-1-ene by an oxygen atom leads to completely different ratios for the modes of addition; the ratio 2,6 : 1,3 changes from 25:75 for benzyl allyl ether to 79:21 for phenethyl vinyl ether[4,5,6].

In 1984 Ellis-Davies et al.[7] have irradiated the three 5-phenylpent-1-enes containing a methyl group at the α, β or γ position. All three compounds give predominantly 2,6 addition next to 1,3 addition; the γ-C derivative gives 2,4 addition additionally. Several compounds with a substituent at the α carbon atom have been irradiated, but in most of these cases an ortho-OCH_3 or -CH_3 group is also present, forcing the addition towards the 1,3 mode[2].

Table 1 Product ratios in the meta photocycloaddition of side-chain methyl-substituted 5-phenylpent-1-enes.

position CH_3	product ratio
α-C	2,6 : 1,3 = 4.5 : 1.0
β-C	2,6 : three minor unidentified isomers = 2.4 : 0.8
γ-C	2,6 : 1,3 : 2,4 = 4.8 : 3.5 : 1.0

Steric constraints have been imposed by using cyclic alkenes, such as 1-(3-phenylpropyl)-1-cycloalkenes or 3-(2-phenethyl)-1-cycloalkenes[7,8]. The quantum yields of 3-(2-phenethyl)-1-cyclopentene and -cyclohexene ($\phi = 0.12$ and 0.15) are quite similar to that of 5-phenylpent-1-ene ($\phi = 0.15$[7]) in which conformational restraints are absent. Apparently the presence of the 5- or 6-membered ring connecting Cγ and Cε of the side chain has little effect on the efficiency of the photoaddition. The benzylic carbon atom of the tether has been restricted in its freedom in 1-(3-butenyl)tetralin[9] and in substituted 1-(3-butenyl)indanes[9,10]. All indane derivatives give 1,3 meta addition next to ortho addition and no 2,6 addition, because the 2,6 adduct would be too strained[9]. Wender et al.[11] have restrained rotation around C14-C1 in the molecule shown in Figure 2a. Although in principle still three modes of addition are possible, only the one across C10 is found, which was indeed

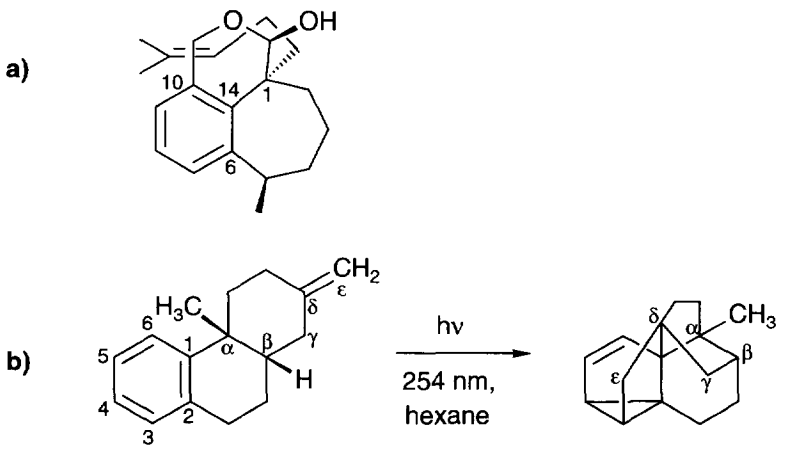
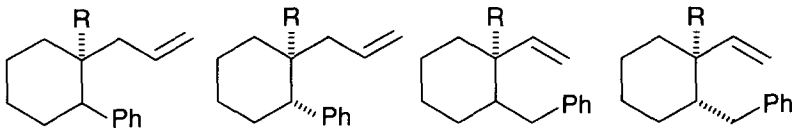


Figure 2 a. Starting material for meta photoaddition towards laurenene. b. Photoaddition of a constrained arene-alkene bichromophoric system[12].

expected to encounter the least steric hindrance. Pallmer and Morrison[12] have restrained the conformational freedom of the tether even further by incorporating the α, β, γ and δ carbon atoms into a decalin (Figure 2b). Only in the cis-decalin the alkene can approach the benzene yielding one 1,3 adduct with 2,4 ring closure. The above studies have shown that subtle changes in the molecular structure can induce steric interactions which have marked effects on the mode of addition.

In order to obtain a more detailed knowledge of the conformational preferences of the tether for the two modes of photoaddition, we have introduced a ring onto the α,β or the β,γ carbon atoms of the tether. Thus, compounds **1** - **9** with a cis or trans connection of the chromophores to the cyclohexane ring and also with a third substituent on Cβ or Cγ of the tether (Figure 3) were synthesized and irradiated. The configuration in the adducts of substituents on the tether is designated as endo or exo, as shown in Figure 1.



1: R = H **2**: R = H **6**: R = H **7**: R = H

3: R = OH **4**: R = OH **9**: R = OH **8**: R = OH

5: R = OCH_3

Figure 3 Compounds irradiated.

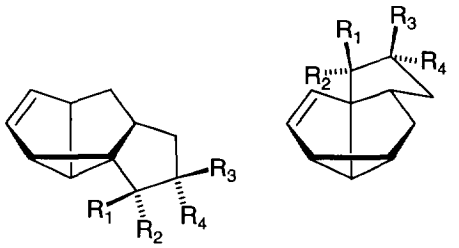
RESULTS

The cycloalkanes

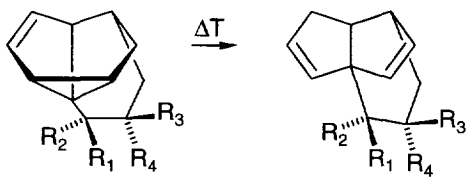
Irradiation of cis-1-allyl-2-phenylcyclohexane (**1**) gave four major photoproducts: both possible rearranged 2,6 adducts **1dx**[13] and **1dy** and 1,3 adducts **1a** and **1b** (Figure 4) in a ratio of 17:8:13:47, determined by analytical GC (AGC). The rearranged 2,6 adducts were obtained because isolation was performed by means of preparative GC (PGC). It is known from the literature that 2,6 adducts undergo a thermal rearrangement via 1,5 H-shift[2]. With the 1,3 adducts both types of ring closure were found, but with only one configuration of the cyclohexane ring fusion as could be deduced from GC analysis and NMR. Apparently, adduct **1b** was converted into **1a** during PGC (ratio 1.2:1) - as is known to occur by means of a vinylcyclopropane-cyclopentene rearrangement[14] -, because during the irradiation the ratio **1a** : **1b** was 1:4 throughout the reaction. During this interconversion the endo/exo substituents at the connecting chain do not change configuration. This means that both adducts, **1a** and **1b**, have the same configuration of the cyclohexane ring fusion, implying that they must have been formed from the same predecessor, i.e. 1,3 addition mode with only one side chain conformation. This configuration (endo or exo) could not be determined, because of the complexity of the sp^3 part of the spectrum.

Irradiation of trans-1-allyl-2-phenylcyclohexane (**2**) on the other hand yielded predominantly 2,6 adducts. The 2,6 adducts, **2dx** and **2dy** (Figure 4), which were isolated in the rearranged form, were present in a ratio of 1.7:1. A linear and an angular 1,3 adduct with the same orientation of the cyclohexane ring were present, **2a** and **2b**, in a ratio of 1.2:1, isolated as a mixture. Adduct **2b** was converted into adduct **2a** near the end of the irradiation via the photochemical vinylcyclopropane-cyclopentene rearrangement[2]. Unfortunately, the configuration of the cyclohexane ring fusion in the adduct could not be determined. The ratio on AGC of the adducts **2dx**, **2dy**, **2a** and **2b** was 39:23:11:9.

Irradiation of cis-1-benzyl-2-vinylcyclohexane (**6**) yielded six photoadducts of which five could be isolated. Only one rearranged 2,6 adduct could be isolated, which was identified as **6dy** (Figure 5), but all four 1,3 adducts were found: **6ax** : **6ay** : **6bx** : **6by**. The ratio of adducts **6dy**, **6ax**, **6ay**, **6bx** and **6by** was 15:24:15:26:10 on AGC.



1a	**1b**	$R_1 + R_3$ or $R_2 + R_4 = -(CH_2)_4-$
2a	**2b**	$R_1 + R_4$ or $R_2 + R_3 = -(CH_2)_4-$
3ax	**3bx**	$R_1 = H$, $R_3 = OH$, $R_2 + R_4 = -(CH_2)_4-$
4ax	**4bx**	$R_2 = H$, $R_3 = OH$, $R_1 + R_4 = -(CH_2)_4-$
5ax	**5bx**	$R_2 = H$, $R_3 = OCH_3$, $R_1 + R_4 = -(CH_2)_4-$



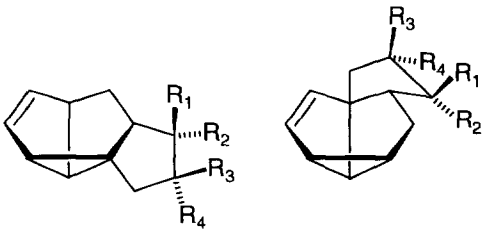
	1dx	$R_2 = R_4 = H$, $R_1 + R_3 = -(CH_2)_4-$
	1dy	$R_1 = R_3 = H$, $R_2 + R_4 = -(CH_2)_4-$
	2dx	$R_1 = R_4 = H$, $R_2 + R_3 = -(CH_2)_4-$
	2dy	$R_2 = R_3 = H$, $R_1 + R_4 = -(CH_2)_4-$
4cx	**4dx**	$R_2 = H$, $R_3 = OH$, $R_1 + R_4 = -(CH_2)_4-$
4cy		$R_1 = H$, $R_4 = OH$, $R_2 + R_3 = -(CH_2)_4-$
	5dy	$R_1 = H$, $R_4 = OCH_3$, $R_2 + R_3 = -(CH_2)_4-$

Figure 4 Photoproducts from compounds **1** - **5**.

Irradiation of trans-1-benzyl-2-vinylcyclohexane (**7**) resulted in six photoadducts. The amount of **7** for irradiation was small (100 mg) and the isolation of the products was troublesome. But both 2,6 rearranged adducts, **7dx** and **7dy** (Figure 5), could be isolated, albeit in one fraction, in a ratio of 3.5:1. Two 1,3 adducts with either ring closure, **7a** and **7b**, were present in a ratio of 1:4 (NMR) in a mixture, which next to the 1,3 adducts (66%) also contained both rearranged 2,6 adducts and the starting material. Again only one isomer of each type of ring closure was identifiable, but their configuration could not be determined. On AGC these two 1,3 adducts had the same retention time, which gives a ratio of 23:46:13 for (**7a+7b**) : **7dx** : **7dy** on AGC.

The oxygen-containing compounds

Irradiation of 1-allyl-t-2-phenyl-1-r-cyclohexanol (**3**) resulted in one major product detectable on AGC. Separation by means of HPLC showed that this peak consisted of two different compounds, in a ratio of 1:1.3, which were identified with NMR as the linear 1,3 adduct, **3ax**, and the angular 1,3 adduct, **3bx** (Figure 4), each



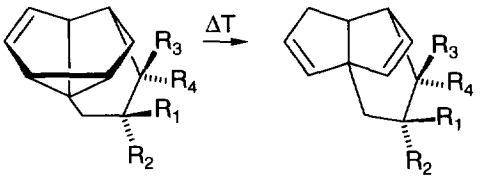
6ax **6bx** $R_2 = R_4 = H$, $R_1 + R_3 = -(CH_2)_4-$

6ay **6by** $R_1 = R_3 = H$, $R_2 + R_4 = -(CH_2)_4-$

7a **7b** $R_1 + R_4$ or $R_2 + R_3 = -(CH_2)_4-$

8ay **8by** $R_2 = OH$, $R_3 = H$, $R_1 + R_4 = -(CH_2)_4-$

9ax **9bx** $R_2 = OH$, $R_4 = H$, $R_1 + R_3 = -(CH_2)_4-$

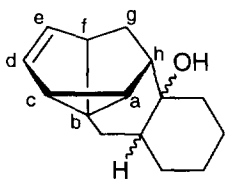


6dy $R_1 = R_3 = H$, $R_2 + R_4 = -(CH_2)_4-$

7dx $R_1 = R_4 = H$, $R_2 + R_3 = -(CH_2)_4-$

7dy $R_2 = R_3 = H$, $R_1 + R_4 = -(CH_2)_4-$

8cy $R_2 = OH$, $R_3 = H$, $R_1 + R_4 = -(CH_2)_4-$



8e

Figure 5 Photoproducts from compounds **6** - **9**.

as a single diastereomer with the OH group endo. The ratio on AGC of **3ax** and **3bx** was 37:48. Irradiation of **3** as a solid gave no products within 24 hours detectable on AGC (except polymer).

Irradiation of 1-allyl-c-2-phenyl-1-r-cyclohexanol (**4**) yielded five photoadducts. One rearranged 2,6 adduct, **4dx** (Figure 4), a linear 1,3 adduct, **4ax**, and an angular 1,3 adduct, **4bx**, could be isolated by means of PGC. By means of HPLC both possible 2,6 adducts, **4cx** and **4cy**, as well as the linear 1,3 adduct **4ax** and the angular 1,3 adduct, **4bx**, could be isolated. The product ratio on AGC of **4dx**, **4cx**, **4cy**, **4ax** and **4bx** was 1:7:1:48:31.

Irradiation of 1-allyl-r-1-methoxy-c-2-phenylcyclohexane (**5**) was stopped after 11 hours because much

polymer was formed, although still 47% starting material was left. Only the two major products could be isolated, each as the major component of a mixture, by PGC: the linear 1,3 adduct, **5ax** (Figure 4) (47%), and the angular 1,3 adduct, **5bx** (68%). Like in the irradiation of the alcohol analogue **4** only one diastereomer of each 1,3 adduct is present with the methoxy group endo. In the fraction containing **5ax** a second compound present for 20% could be identified as a 2,6 adduct. It appeared to be **5dy** from comparison with some proton resonances of adducts **2dx** and **4dx**. On AGC the adduct ratio of **5dy**, **5ax**, **5bx** and **5cy** was 1:20:26:2.

Irradiation of c-2-benzyl-1-vinyl-r-1-cyclohexanol (**8**) yielded seven products. Four of these products could be isolated by means of HPLC. One 2,6 adduct could be identified in a fraction containing also the starting material, as **8cy** (Figure 5). Two other fractions were isolated as white solids; these appeared to be the 1,3 adducts **8ay** and **8by** with the OH group exo as identified by means of NMR. The structure of **8by** was confirmed by X-ray analysis[15] (Figure 6). The first fraction on HPLC (eluting on AGC together with **8ay**) appeared to be an unusual 2,6 adduct, probably with structure **8e**. The analytical ratio of **8ay** : **8by** : **8cy** : **8e** = 26:36:1:21 (with 4% of **8dy**).

Irradiation of t-2-benzyl-1-vinyl-r-1-cyclohexanol (**9**) yielded two photoproducts isolated by HPLC: a linear 1,3 adduct, **9ax** (Figure 5), and an angular 1,3 adduct, **9bx**, in a ratio of 49:34, both with the OH group exo, which is consistent with their interconvertibility during longer irradiation times.

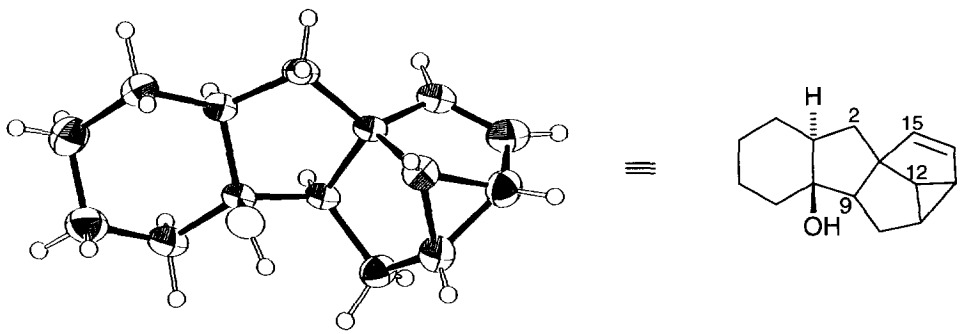


Figure 6 X-ray structure of **8by**.

CHARACTERIZATION OF THE ADDUCTS

The determination of the structures of the photoadducts was based chiefly on 1D and 2D NMR spectra. The differentiation between 2,6 adduct, angular and linear 1,3 adduct was relatively simple, because of their own characteristic features of the tricyclo[3.3.0.$0^{2,8}$]oct-3-ene unit which are well known from the literature, inter-[16] as well as intramolecular[8,10,17,18]. Connectivities of the protons were determined by decoupling, 2D COSY and J-Resolved 2D ^{1}H NMR experiments. The proximity of protons was resolved performing nuclear Overhauser enhancement measurements. The assignments of the carbon atoms were obtained from ^{13}C APT (Attached Proton Test) and ^{1}H-^{13}C COSY measurements. The structure of three of the hydroxyl containing 1,3 adducts was confirmed by means of Eu(FOD)$_3$-complex measurements. In cases of doubt concerning the configuration of the cyclohexane ring fusion, coupling constants were calculated using Model[19].

The resulting chemical shifts and ^{3}J coupling constants of the skeletal protons for the four types of adducts, i.e. **a**, **b**, **c** and **d**, are given in Tables 2, 3, 4 and 5, respectively. For the sake of comparison the atoms are indicated with a letter (Figure 7), because adducts of different types have different IUPAC numbering. Endo

protons are designated with H_a and exo protons with H_b.

The configuration of the cyclohexane ring fusion of the 1,3 adducts formed from compounds **1**, **2** and **7** could not be determined, because the linear and angular adducts appeared in the same fraction on PGC. It could be established, however, that from each of the three starting materials one angular and one linear 1,3 adduct are formed (characteristic features of the 1,3 adducts).

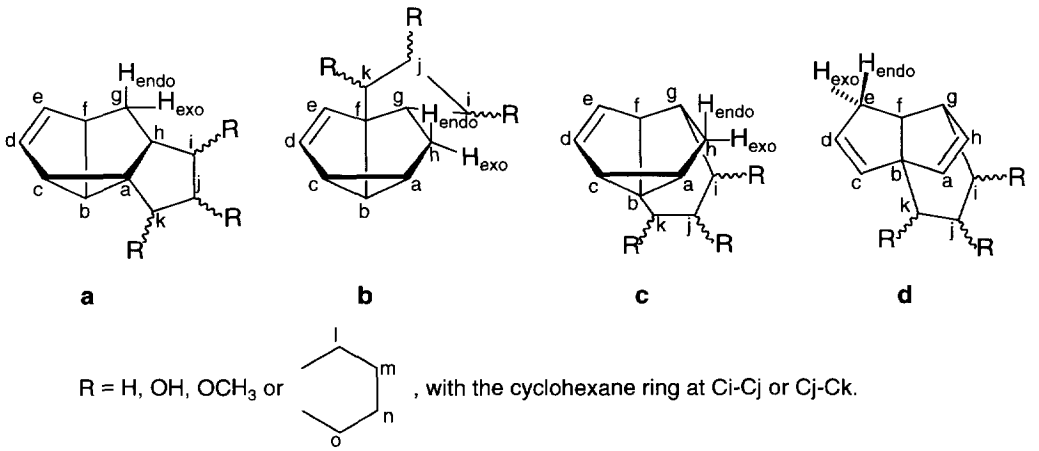


Figure 7 Lettering of the photoadducts.

The structure of the isolated, unusual 2,6 adduct, **8e** is not presented in the Tables, but will be treated here. Its NMR spectrum has the typical two double doublets of the olefinic protons of a meta adduct and five CH and six CH_2 signals are present in the sp^3 region as well as two CH signals in the sp^2 region of the APT ^{13}C spectrum. Each olefinic proton couples with a tertiary sp^3 proton, at 2.78 and 1.62 ppm, respectively, with a normal coupling of 2.5 and 2.2 Hz, respectively. Proton Hf at 2.78 ppm couples (6.6 Hz) with a proton at 1.88 ppm, which is part of a CH_2 group and not with a cyclopropane ring proton. Moreover, proton Hc at 1.62 ppm couples with one other cyclopropane ring proton at 1.46 ppm, with a coupling constant of 7 Hz. This means that Cb must be quaternary, which yields one connection of the chain. Because Hf couples with a CH_2 proton, which must be at Cg, the other connection of the chain must be at Ch. Therefore the adduct is tentatively assigned structure **8e**, a 2,6 adduct with the unusual 1,3 cyclopropane ring closure. This type of adduct has been reported before by Gilbert et al.[7] from 3-methyl-5-phenylpent-1-ene and 5-methyl-5-phenylpent-1-ene. Their structure assignment was also tentative and the adducts were contaminated with other products.

DISCUSSION

For the reaction to be successful, the aromatic part of the molecule and the alkene moiety must be able to approach each other and to interact with their π-orbitals within the lifetime of the excited state. The restrictions imposed by the cycloalkane on the mobility of the side chain connecting the phenyl ring and the alkene evidently are not so severe that the reaction is inhibited.

Table 2 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **a**.

adduct	R_1	R_2	Hb	Hc	Hd	He	Hf	Hg_a	Hg_b	Hh	Hi_a	Hi_b	Hj	Hk_a	Hk_b	Other protons
1a	ring		2.38	1.86	5.61	5.40	3.22	1.75	1.69	2.20	-	-	-	-	-	2.1-1.2
2a	ring		2.06	1.96	5.57	5.43	3.26	-	-	-	-	-	-	-	-	2.3-0.9
3ax	OH	ring	2.38	1.95	5.66	5.44	3.24	1.78	1.67	2.44	1.74	1.73		1.7-1.5		1.9 (m, Hl_{eq}); 1.55 (ddd, Hl_{ax}, J=13.0,10.3,3.8); 1.7-1.5 and 1.45-1.05
4ax	OH	ring	2.08	1.98	5.62	5.47	3.30	1.79	1.72	2.45	1.99	1.31			1.85	1.86(m, Hl_{eq}); 1.42 (dt, Hl_{ax}, 2x12.8,4.5); 1.7-1.45 and 1.3-1.1
5ax	OCH_3	ring		1.98	5.65	5.44	3.28	-	-	-	-	-			-	3.11(s, OCH_3); 2.5-0.9
6ax	ring	H	2.14	1.95	5.64	5.37	3.12	1.78	1.70	1.86		1.62	2.28	1.81	1.27	
6ay[a]	H	ring	2.2	1.82	5.60	5.41	3.23	-	-	-	-		-	-	-	2.2-1.15
7a	ring		-	-	5.59	5.41	3.26	-	-	-	-	-	-	-	-	2.05-0.7
8ay	H	ring	2.27	1.84	5.58	5.45	3.33	1.37	2.16	2.11			1.87	1.50	1.70	1.8-1.1
9ax	ring	H	2.20	1.92	5.62	5.40	3.22	1.53	2.09	2.00			2.10	1.72	1.49	1.7-1.4

			b,c	b,f	c,d	d,e	e,f	f,g_b	g_a,h	g_b,h	h,i_a	h,i_b	i_a,j	i_b,j	j,k_a	j,k_b	Other couplings
1a	ring		6.5	5.4	2.2	5.3	2.3	4.9	6.4	9.1	6.9*	8.8*	-	-	ring/ -		
2a	ring		6.1	7.0	2.1	5.4	2.3	4.2	-	-	-	-	-	-	ring/ -		
3ax	OH	ring	6.7	5.3	2.1	5.4	2.4	5.3	6.2	9.9	8.6*	8.2*					c,e=+; c,g_a=+
4ax	OH	ring	6.5	5.2	2.1	5.4	2.3	5.2	6.5	10.0	7.4	10.0					
5ax	OCH_3	ring	6.6	5.6	2.1	5.4	2.5	5.6	-	-	-	-					
6ax	ring	H	6.4	5.3	2.2	5.4	2.4	5.0	6.2	9.6		3.3		-	9.1	6.0	d,f=+; b,e=+; b,g_b=+; c,e=1
6ay[a]	H	ring	-	6.6	2.1	5.4	2.4	6.6	-	-	-		-		-	-	
7a	ring		-	5.8	2.2	5.4	2.3	5.8	-	-	ring/ -		ring/ -		-	-	
8ay	H	ring	6.3	5.3	2.1	5.3	2.4	5.3	5.6	9.3					6.8	12.2	
9ax	ring	H	6.2	5.6	2.2	5.4	2.4	5.4	5.6	10.0					8.8	-	c,f=+

* indicates that these values may be interchanged

\+ indicates that coupling is present, but its magnitude could not be determined owing to the complexity of the spectrum and/or because it was too small

[a] Of this compound only a few protons were identified from the 8% **6ay** present within **6by** (the fraction containing mainly **6ay** was lost before NMR)

Table 3 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **b**.

adduct	R_1	R_2	Ha	Hb	Hc	Hd	He	Hg	Hh_a	Hh_b	Hi_a	Hi_b	Hj	Hk_a	Hk_b	Other protons
1b	ring		1.65	2.48	1.76	5.54	5.31	2.27	-	-	-	-	-	ring/ -		2.1-1.2
2b	ring		1.75	2.24	1.62	5.51	5.48	-	-	-	-	-	-	ring/ -		2.3-0.9
3bx[a]	OH	ring	1.63	2.43	1.78	5.56	5.36	2.30	-	-	-	1.69		1.89		1.8-1.4
4bx	OH	ring	1.80	2.30	1.60	5.52	5.52	2.60	2.05	1.85	1.54	1.45			1.6	1.85-1.4 and 1.35-1.2
5bx	OCH_3	ring	1.78	2.27	1.58	5.48	5.54	2.34	2.01	1.83	1.81	1.14			-	3.01 (s, OCH_3); 2.1-1.1
6bx	ring	H	1.63	2.26	1.76	5.49	5.39	-	1.92	2.12		-	2.06	1.40	2.01	1.7-1.35 and 1.2-0.95
6by	H	ring	1.68	2.28	1.74	5.46	5.48	2.22	1.74	1.92	1.53		2.24	1.83	1.71	1.8-1.25
7b	ring		1.67	2.24	1.77	5.48	5.41	-	-	-	ring/ -			-	-	2.05-0.7
8by	H	ring	1.83	2.33	1.78	5.51	5.49	1.92	1.79	2.04			1.64	1.98	1.52	1.73 (m, Ho_{eq}); 1.8-1.45; 0.98 (dt, Ho_{ax}, 2x12.3,4.8)
9bx	H	ring	1.83	2.39	1.80	5.53	5.46	2.40	1.80	1.98			2.01	1.51	2.22	1.70 (m, Ho_{eq}); 1.75-1.55 and 1.4-1.1; 0.98 (dq, Ho_{ax}, 3x12.5,2.5)

adduct	R_1	R_2	a,b	a,c	a,h_a	a,h_b	b,c	c,d	d,e	g,h_a	g,h_b	g,i_a	g,i_b	i_a,j	i_b,j	j,k_a	j,k_b	Other J
1b	ring		6.2*	-	-	-	7.1*	2.2	5.3	-	-	-	-	-	-	ring/ -		
2b	ring		6.7	6.9	-	-	6.8	2.0	5.3	-	-	-	-	-	-	ring/ -		c,e=0.6
3bx[a]	OH	ring	6.8	6.8	0.0	4.9	6.3	2.3	5.4	7.9	0.0	5.7	11.2					k,o_{ax}=9.2; k,o_{eq}=6.1; b,e=+; c,e=+
4bx	OH	ring	6.4	6.4	0.0	6.4	6.4	+	0.0	7.8	1.8	6.6	12.0					
5bx	OCH_3	ring	6.3	7.1	0.0	6.4	6.8	2.2	5.2	7.9	1.8	6.5	12.5					b,e=+
6bx	ring	H	6.7	6.7	1.9	5.1	6.7	2.2	5.3	6.4	1.5		-		-	1.5	7.8	b,e=+; c,e=+; e,g=+
6by	H	ring	6.8	7.1	1.0	6.3	6.8	2.0	5.2	7.7	1.4	-		-		9.3	11.8	b,e=+
7b	ring		6.7	6.7	-	-	6.7	2.1	5.3	-	-	ring/ -		ring/ -		-	-	
8by	H	ring	6.7	6.7	1.0	6.5	6.7	2.0	5.2	8.0	1.2					7.5	11.4	b,e=+
9bx	H	ring	6.7	6.7	0.0	6.7	6.7	2.0	5.2	7.1	+					1.3	7.5	j,o_{eq}=6.0; b,e=+; c,e=+

[a] 400 MHz

* indicates that these values may be interchanged

\+ indicates that coupling is present, but its magnitude could not be determined owing to the complexity of the spectrum and/or because it was too small

Table 4 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **c**.

adduct	R_1	R_2	Ha	Hc	Hd	He	Hf	Hg	Hh_a	Hh_b	Hi_a	Hi_b	Hj	Hk_a	Hk_b	Other protons
2cx[a]	ring	H	0.87	2.48	5.66	5.59	2.26	2.44	-	-	-	-	-	-		
2cy[a]	H	ring	0.80	2.53	5.64	5.45	2.82	2.40	-	-	-	-	-		-	
4cx[b]	OH	ring	1.53	2.32	5.71	5.48	2.32	2.39	1.60	1.95	1.81*	1.71*			2.23	1.4 (m, Ho_{ax} and Ho_{eq}); 1.75-1.5 and 1.45-1.3
4cy	ring	OH	0.79	2.64	5.64	5.51	3.64	2.47	1.42	1.52	1.58	2.00		-		1.8-1.3
8cy	H	ring	0.75	2.62	5.72	5.56	2.98	2.14	1.50	1.71			1.72	1.47	1.93	1.7-1.2

			a,c	a,h_a	a,h_b	c,d	d,e	e,f	g,h_a	g,h_b	g,i_a	g,i_b	i_a,j	i_b,j	j,k_a	j,k_b	Other J
2cx[a]	ring	H	6.5	3.1	6.5	2.4	6.0	2.3	-	-	-	8	-	-	-		
2cy[a]	H	ring	6.3	3.3	6.3	2.4	6.1	2.2	-	-	-	-	-	-		-	
4cx	OH	ring	6.3	2.4	6.3	2.5	5.8	2.5	3.2	2.8	2.8	3.1					k_b,o_{ax}=10.7; k_b,o_{eq}=4.3; c,e=0.9; c,f=2.5
4cy	ring	OH	6.5	2.9	6.5	2.5	5.8	2.6	2.9	0.0	1	8.4					f,h_b=2.6; c,f=2.3; c,e=1
8cy	H	ring	6.5	2.8	6.5	2.3	5.8	2.6	3.4	2.8					5.2	10.4	c,f=2.6; f,g=+

[a] from NMR of the irradiation mixture

[b] 400 MHz

* indicates that these values may be interchanged

+ indicates that coupling is present, but its magnitude could not be determined owing to the complexity of the spectrum and/or because it was too small

Table 5 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **d**.

adduct	R_1	R_2	Ha	Hc	Hd	He_a	He_b	Hf	Hg	Hh	Hi_a	Hi_b	Hj	Hk_a	Hk_b	Other protons
1dx	ring	H	5.36	5.97	5.77	2.00*	2.28*	1.91	2.58	5.67	1.29	1.82	-		-	2.0-1.4 and 1.3-1.1
1dy	H	ring	5.26	5.75 -	5.68	1.94*	2.22*	2.24	2.62	5.67	1.19	1.40	2.01	1.72		1.70(m); 1.55-1.4 and 1.3-1.05
2dx	ring	H	5.38	5.91	5.75	1.89*	2.22*	2.79	2.53	5.87	1.09	1.66	1.72	1.34		1.75 (m,Ho_{eq}); 1.8-1.6; 1.50 (double m, J=12.5); 1.3-0.9
2dy	H	ring	5.29	5.92	5.75	1.98*	2.25*	1.79	2.62	5.72	1.44	1.05	1.25		-	1.8-1.5 and 1.3-0.95
4dx	OH	ring	5.61	5.90*	5.80*	1.97*	2.32*	2.05	2.71	6.15	1.87	1.63			1.6	3.13 (d, OH, J=2.7), 1.8-1.2; 1.12 (ddt,Ho_{ax}, J=2x12.8,4.3,2.7)
5dy	ring	OCH_3	5.47	5.92	5.75	-	-	3.63	-	5.88	-	-		-		3.07 (s, OCH_3); 2.0-0.9
6dy	H	ring	5.24	5.78	5.73	1.94*	2.19*	2.11	2.43	5.70	1.52		2.01	1.44	1.33	1.70 (m); 1.6-1.4 and 1.25-1.1
7dx	ring	H	5.32	5.80	5.74	1.90*	2.19*	2.74	2.10	5.98	1.20		1.73	1.24	1.60	1.8-1.0
7dy	H	ring	5.29	5.78	5.73	1.99*	2.22*	1.79	2.35	5.67		-	1.23	1.65	0.94	1.8-1.0

			a,h	c,d	c,e_a	c,e_b	d,e_a	d,e_b	e_a,f	e_b,f	g,h	g,i_a	g,i_b	i_a,j	i_b,j	j,k_a	j,k_b	Other J
1dx	ring	H	5.5	5.7	2.8	1.2	1.6	2.8	9.2	6.9	2.8	3.0	2.9	0.0	7.8		-	
1dy	H	ring	5.4	-	2.6	0.7	1.5	2.3	11.3	7.7	2.8	2.6	2.6	-	12.5	4.9		k,o_{ax}=12.2; k,o_{eq}=4.9;
2dx	ring	H	5.3	5.7	2.9	1.3	1.8	2.8	8.5	7.9	2.9	0.0	7.6	10.8	-	10.2		k,o_{ax}=12.6; k,o_{eq}=2.9; f,h=0.7; a,f=+
2dy	H	ring	5.6	5.7	2.9	1.2	1.7	2.8	9.2	7.6	2.7	3.6	1.9	5.3	10.8		-	
4dx	OH	ring	5.7	5.7	+	2.8	2.9	1.6	6.1	9.2	2.4	3.4	2.5					
5dy	ring	OCH_3	5.4	5.8	-	-	2.8*	1.8*	8.6*	8.0*	2.8	-	-					f,h=0.6
6dy	H	ring	5.6	5.7	2.7	1.1	1.5	2.7	6.6	7.3	2.4	2.4		-		6.4	12.3	c,g=+; f,h=0.6; f,k_b=+
7dx	ring	H	5.4	5.7	2.9	1.2	1.6	2.8	8.7	7.8	2.9	0.0		-		11.0	7.6	
7dy	H	ring	5.5	5.8	2.7	1.2	1.6	2.8	8.8	7.9	2.8		-		-	5.3	11.0	a,g=0.7

* indicates that these values may be interchanged

\+ indicates that coupling is present, but its magnitude could not be determined owing to the complexity of the spectrum and/or because it was too small

The presence of the cycloalkane ring has an effect on the ratio of 2,6 vs. 1,3 adducts. For the parent compound, 5-phenylpent-1-ene (**P**) and the cyclohexane derivatives (**1** - **9**) mentioned above these ratios are presented in Table 6.

Table 6 Percentages of 2,6 and 1,3 photoaddition for 5-phenylpent-1-ene (**P**)[7] and compounds **1** - **9** (normalized to 2,6 + 1,3 = 100 %).

starting material	% 2,6 addition	% 1,3 addition	2,6 : 1,3
P	72	28	2.6 : 1
1	29	71	1 : 2.4
2	76	24	3.2 : 1
3	0	100	0 : 1
4	9	91	1 : 10
5	6	94	1 : 16
6	17	83	1 : 4.9
7	72	28	2.6 : 1
8	30	70	1 : 23
9	0	100	0 : 1

The differences in the 2,6 : 1,3 ratios seem large; but in terms of energy differences they correspond to less than 1.6 kcal/mol. The variations in the ratios must be due to subtle geometrical differences, because the ten molecules in Table 6 are electronically very similar. The possibilities for photoaddition were examined by inspecting molecular models (Molecular Visions, Darling Models; Stow, Ohio, U.S.A. and Dreiding Stereomodels, W. Büchi, Flawil, Switzerland), but it is known that the benzene ring becomes more flexible upon excitation to the singlet excited state and this may influence the possibilities of approach of the addends.

The cycloalkane compounds

The preponderance of 2,6 addition in the case of 5-phenylpent-1-ene is ascribed to stabilization by the alkyl group of the positive charge that develops on carbon atom 1 of the phenyl ring in the initial stage of the reaction. Compounds **2** and **7** have the same 2,6 : 1,3 ratio as 5-phenylpent-1-ene. They also both have a trans substituted cyclohexane ring and apparently this has the same effect on 2,6 as on 1,3 approach or no effect at all.

From **2** and **7** both possible 2,6 adducts are formed, but only one diastereomer of each of the 1,3 adducts. From molecular models it can be seen that both 2,6 addition modes (2,6A and 2,6B) are equally hindered for compound **2** (see Figure 8), while the 1,3B mode of addition is evidently sterically more favoured than the other three modes. Therefore the adducts **2a** and **2b** probably have the configuration with Hk exo and Hj endo. The adducts **2dx** and **2dy** are formed in a ratio of 39 : 23 from the conformations 2,6A and 2,6B, respectively.

In the 2,6A conformation of **7** (Figure 9) the constraint imposed by the cyclohexane ring makes it difficult for the alkene to attain the right position above carbon atoms 2 and 6 of the benzene ring. Nevertheless, this mode of addition, which leads to **7dx**, prevails over the other ones. Interestingly, in the 2,6A mode of approach the hydrogen atoms of the benzylic CH_2 group and the substituents at C1 of the cyclohexane ring are staggered, while in 2,6B they are rather eclipsed. In the 1,3A conformation the alkene also cannot move to the proper

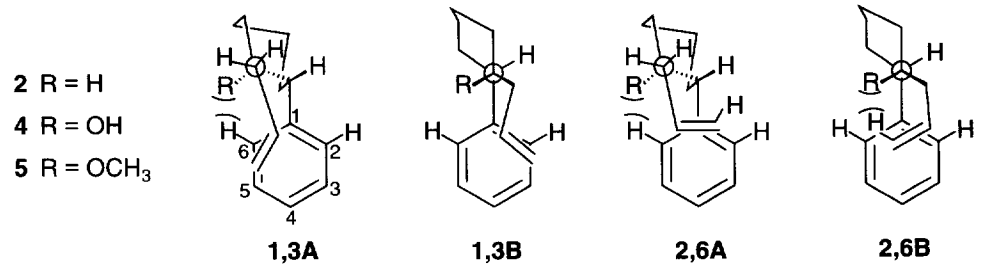


Figure 8 Modes of addition of **2**, **4** and **5**.

position above the benzene ring, as in the 2,6A addition. On the other hand, in 1,3B the approach is much easier and there seems to be little steric hindrance. But only speculations can be made about the configuration of the cyclohexane ring fusion in the products found, **7a** and **7b**.

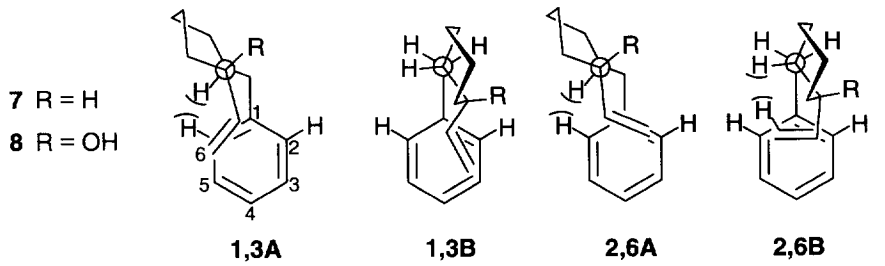


Figure 9 Modes of addition of **7** and **8**.

Compounds **1** and **6** have a cis fused cyclohexane ring and this appears to disfavour 2,6 addition. In the addition mode 2,6A of compound **1** (Figure 10) there is steric hindrance between the ortho aromatic hydrogen atom H6 and the cyclohexane hydrogen atom H3ax. Perhaps most importantly there is also interaction between

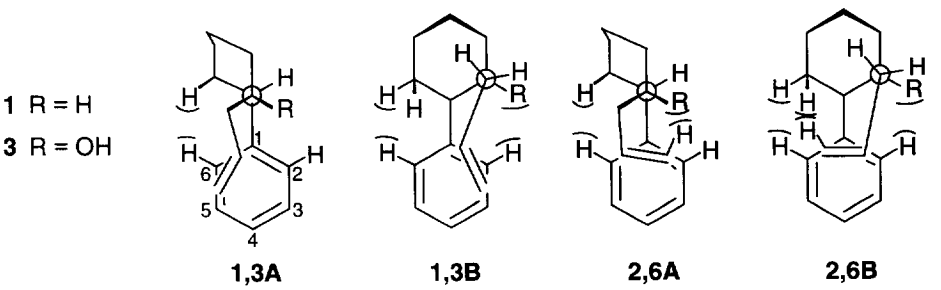


Figure 10 Modes of addition of **1** and **3**.

the exo vinyl hydrogen atom and the axial cyclohexane hydrogen atom H1. This addition mode leads to **1dy**, the minor (rearranged) 2,6 adduct. The 2,6B mode of addition, which leads to **1dx**, has the phenyl group and the cyclohexane ring in the same plane, which leads to steric interaction between H6 of the phenyl ring and H3eq as well as between H2 of phenyl and H1eq. The exo vinyl hydrogen atom is close to the cyclohexane hydrogen atom H3ax. In the 1,3B conformation the phenyl ring and the cyclohexane ring are in the same plane

with the same consequences as in 2,6B. The 1,3A mode, however, appears to be relatively unhindered and seems favoured over the 1,3B mode. It is perhaps significant that in this approach the conformation of the hydrogen atoms of the allylic CH_2 group and the substituents at C1 of the cyclohexane ring is staggered. This approach leads to a configuration of **1a** and **1b**, in which Hk and Hj are endo; again only one diastereomer is formed.

From inspection of molecular models it is clear that of the four hydrocarbons **6** is the one with the least tendency to undergo 2,6 addition (see Figures 8-11). The 2,6 adduct found, **6dy**, is formed via the 2,6B approach, which might be caused by the fact that the benzylic hydrogen atoms and the substituents at C1 of the cyclohexane ring are less staggered in the 2,6A mode than in the 2,6B mode of addition. In the 1,3B mode there is interference between the exo vinyl hydrogen atom and H4ax as well as between H2 of the phenyl group and H6ax. The 1,3A mode appears to have much less steric hindrance and, indeed, the adducts formed via this mode, **6ax** and **6bx**, are found in larger amounts than the ones, **6ay** and **6by**, formed via the unfavourable 1,3B mode. It is hard to understand why adducts are formed via this mode at all, even if the possibility of the occurrence of the conformation with benzyl axial and vinyl equatiorial is taken into account.

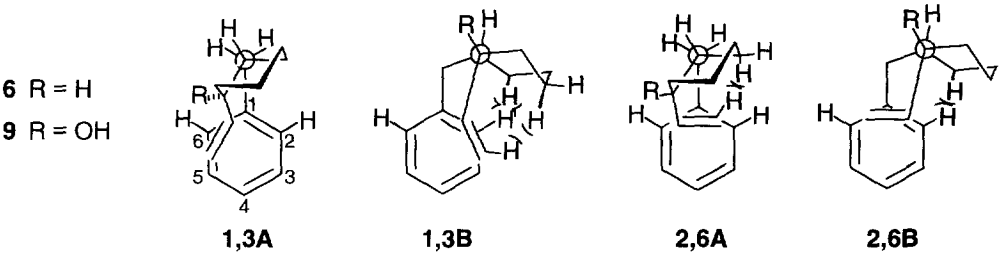


Figure 11 Modes of addition of **6** and **9**.

The oxygen-containing compounds

Introduction of a hydroxyl group at position 1 in compound **2** leads to increase of steric hindrance in the 2,6A as well as in the 2,6B mode (Figure 8). As a result the relative amount of 2,6 adducts from compound **4** is drastically lower than that from compound **2**. Surprisingly, the small amount of 2,6 adduct that is still formed originates predominantly from the 2,6B mode of approach, which seems to be even more hindered than 2,6A. The preference for 1,3B addition seen in compound **2** is also present in compound **4** and this mode gives rise to adducts **4ax** and **4bx** with endo OH at Cj and exo H at Ck.

Preponderance of 1,3 addition is also seen in compound **5**, which has a methoxy group at C1 and otherwise the same structure as **4**. The configuration at Ck and Cj of the 1,3 adducts from **5** is the same as in those from **4**. The very small amount of 2,6 adduct, **5dy**, has been formed via addition mode 2,6A, which indeed seems to be less hindered than 2,6B (Figure 8).

The 1,3 adducts formed from compound **8**, **8ay** and **8by**, result from the 1,3B mode of addition (Figure 9), although the steric hindrance between the OH group and H6 of the phenyl ring is appreciable. Introduction of the OH group gives additional steric hindrance in both 2,6 addition modes compared to compound **7**, but the 2,6 adduct found, **8cy**, is the one from 2,6B addition, while in the hydrogen analogue **7** the 2,6A mode of addition predominates. Even more surprisingly, another 2,6 adduct with unusual cyclopropane ring closure (**8e**) was found. Unfortunately, the configuration at the cyclohexane ring fusion could not be determined.

The steric hindrance already present in both 2,6 modes of compounds **1** and **6** is increased even further in compounds **3** (Figure 10) and **9** (Figure 11), respectively, with an additional OH group at C1. The result is that 2,6 addition is no longer found. The 1,3A mode, leading to adducts with an exo OH group, is sterically less hindered than the 1,3B mode in compound **3** as well as **9**, and indeed, the products found, **3ax**, **3bx**, **9ax** and **9bx**, are formed via this approach. However, upon comparing compounds **6** and **9**, the introduction of an OH group only adds steric hindrance to 1,3A and not to 1,3B, so some electronic factor must eliminate conformation 1,3B which is still present in compound **6** and the only 1,3 adducts found are **9ax** and **9bx** with exo OH at Ci.

Conclusions

From the results described above it is clear that the configuration at the ring (cis or trans allyl and phenyl or vinyl and benzyl) is a factor of importance in determining the regiochemistry of the process (2,6 vs. 1,3 addition) and not the position of the ring on the chain. The trans-1,2-disubstituted cycloalkanes (**2** and **7**) give mostly 2,6 addition and the 2,6 : 1,3 ratios do not differ much from that of 5-phenylpent-1-ene. Cis-disubstituted cyclohexanes (**1** and **6**) give more 1,3 than 2,6 addition. All modes of addition for each of the compounds have the same number of gauche interactions.

In the trans compounds only three of the four addition modes suffer from steric hindrance between two groups, while the 1,3B mode has no steric hindrance at all. Obviously, this steric hindrance is not sufficient to counteract the stabilizing effect of the alkyl group in 2,6 addition. The 2,6 addition modes in the cis compounds have either steric interactions at several positions (compound **1**) or severe steric hindrance (compound **6**), while again one of the 1,3 modes, 1,3A, has steric interaction at only one position (**1**) or no steric hindrance (**6**) resulting in more 1,3 than 2,6 addition.

A striking analogy is seen in the conformation of the connecting chain leading to addition (Figures 8-11). For 2,6 addition two basic conformations of the connecting chain seem to be possible: a conformation with the β-carbon pointing towards the exo vinyl carbon (conformation **A** in Figure 12) and a conformation with the β-carbon pointing away from the double bond (conformation **B**). For 2,6 addition in compounds **1**, **2**, **5**, **6** and **7** conformation **B** dominates. Both conformations leading to 2,6 addition suffer from steric hindrance: in conformation **A** there is steric interaction between a β-hydrogen atom and the alkene, while in conformation **B** steric hindrance occurs between a β-hydrogen atom and an ortho hydrogen atom (Figure 12). But, except for **1**, conformation **B** has more staggered Cα-Cβ and Cβ-Cγ bonds than **A**. The importance of the conformation of the connecting chain in terms of staggering and eclipsing interactions has been noticed by Gilbert et al.[4].

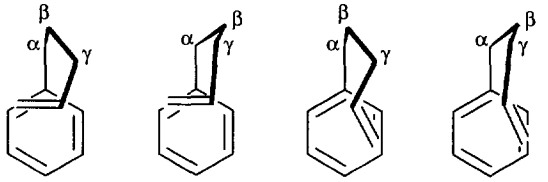


Figure 12 Conformations leading to 2,6 and 1,3 addition.

Only introduction of a hydroxyl group as in compounds **4** and **8**, but not a methoxy (**5**), renders conformation **A** more favourable, which must be caused by an electronic factor, which stabilizes conformation **A** or destabilizes **B**.

In the 1,3 addition of compounds **3**, **4**, **5**, **6**, **8** and **9** a preference is observed for formation of adducts via the conformation with the β-carbon atom away from the alkene (see Figure 12, **C**). From molecular models it can be seen that the same preference is present in conformations leading to 1,3 addition of compounds **1**, **2** and probably **7**. In conformation **D** leading to 1,3 addition the same type of interaction is present as in **B** for 2,6 addition, while conformation **C** lacks steric hindrance. This is obviously the driving force for 1,3 addition to occur via conformation **C**.

From the results it can be concluded that steric interactions are only able to influence the ratio of the two modes of 2,6 addition and that of 1,3 vs. 2,6 addition, not the ratio of the two modes of 1,3 addition (except for **6**). This means that the free energy difference between 1,3 and 2,6 addition must be smaller than the difference between the modes of 1,3 addition.

The introduction of a third substituent, OH or OCH_3, shifts the ratio 2,6 : 1,3 in favour of 1,3 addition to such an extent that in some cases (compounds **3** and **9**, with cis aryl and alkenyl) only 1,3 addition is observed. Introduction of OH or OCH_3 at position 1 in trans-1-allyl-2-phenylcyclohexane reverses the 2,6 : 1,3 ratio from 76 : 24 (**2**) to 9: 91 (**4**) or 6 : 94 (**5**). So if only steric factors are important in determining the 2,6 : 1,3 ratio the 2,6 addition is obviously the most susceptible to steric hindrance.

Because in the cycloalkane derivatives the presence of the extra substituent at one of the positions β or γ of the chain connecting phenyl ring and alkene causes such strong preference for 1,3 addition and some preferences for addition modes are unexpected on the basis of steric considerations only, it will be of interest to investigate whether substituents at the connecting chain in 5-phenylpent-1-ene have similar effects. Results will be published in our next article.

EXPERIMENTAL DETAILS

The starting materials for the synthesis of the compounds were purchased from Aldrich Chemicals N.V., Belgium, Janssen Chimica, The Netherlands, and Fluka Chemika, Switzerland. Dry solvents were distilled prior to use: diethyl ether (ether) and THF were distilled from lithium aluminium hydride and pyridine from barium oxide. Petroleum ether with a boiling range of 40 - 60 °C was used. Column chromatography was performed on Merck (230 - 400 mesh) silicagel. For the syntheses analytical gas chromatography was performed on a Packard 433 GC (column: OV101, 25m, carrier gas H_2). Preparative gas chromatography was performed on a Varian Aerograph 90-P (glass column, 6 m x 8 mm, 20% SE 30 on Chromosorb WAW mesh 40 - 60, carrier gas H_2).

^1H NMR spectra were recorded on a Jeol FX-200 at 200 MHz (for intermediates) or a Bruker WM300 spectrometer at 300 MHz (for end products) in $CDCl_3$ using tetramethylsilane (TMS, 0 ppm) as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz (derived from first order analysis). NOE experiments were carried out with solutions purged with argon. In the presentation of the NMR data the proton saturated in the experiment is followed between parentheses by the protons on which an effect has been measured. ^{13}C NMR spectra were recorded on a Bruker WM300 spectrometer at 75.5 MHz. The IR spectra were recorded on a Pye-Unicam SP3-200 spectrometer and the UV spectra on a Varian DMS-200 spectrometer.

Irradiations were carried out in quartz vessels in a Rayonet Photochemical Reactor RPR 200 fitted with eight 254 nm lamps, placed in a room cooled to 4°C. All irradiations (1% w/v solutions) were performed in commercially available cyclohexane (Uvasol, Merck) under argon atmosphere.

Analysis of the irradiation mixtures was performed on a Varian 3400 Gas Chromatograph (OV101, 25m, carrier gas H_2). The photoproducts of compounds **1**, **2** and **4** - **7** were separated on a Varian Aerograph model 90P with H_2 as carrier gas. The columns used are: 15% SE-30 on Chromosorb WAW, 45-60μ, 6m x 8mm for compounds **2** and **5**; 15% OV17 on Chromosorb WAW, 45-60μ, 6m x 8mm for compounds **1** and **4**; 15% Carbowax on Chromosorb WAW, 45-60μ, 6m x 8mm for compounds **6** and **7**. The photoproducts of compounds **3**, **4**, **8** and **9** were isolated by means of HPLC with an LKB Bromma 2151 pump or a Micromeritics Liquid Chromatograph model 7000B pump equipped with an LKB Bromma variable wavelength detector and a Zorbax Sil column (DuPont), 2.1 x 25 cm.

^1H NMR spectrometry was performed on a Bruker WM300 or a Bruker MSL400 operating at 300 or 400 MHz. ^{13}C NMR was performed on a JEOL FX200, a Bruker WM300 or a Bruker MSL400 operating at 50.1 MHz, 75.5 MHz or 100 MHz, respectively. All spectra were recorded in $CDCl_3$ with TMS as internal standard. Connectivities of the protons

were determined by decoupling, 2D COSY and J-Resolved 2D ^{1}H NMR experiments. The proximity of the protons was obtained by nuclear Overhauser enhancement measurements (see above). The assignments of the carbon atoms were obtained from ^{13}C APT (Attached Proton Test) and ^{1}H-^{13}C COSY measurements. Sometimes insufficient material (< 10 mg) was isolated to measure ^{13}C spectra. Eu(FOD)$_3$ was obtained from Merck. Chemical shifts marked with an asterisk may be interchanged. The numbering of the adducts is following the Von Baeyer system from the IUPAC rules. The endo and exo hydrogen atoms are indicated with Ha and Hb, respectively.

The EI (or CI(NH_3)) mass spectra were recorded on a Finnigan MAT 900 mass spectrometer.

Synthesis of the starting materials

Cis- and trans-1-allyl-2-phenylcyclohexane (1 and 2)

Trans-2-phenylcyclohexanol (I): Addition of 13.0 g (0.13 mol) cyclohexene oxide to phenylmagnesium bromide, prepared from 4.7 g (0.19 mol) magnesium turnings, 30.3 g (0.19 mol) bromobenzene and 3.7 g (0.019 mol) copper iodide, in THF, afforded trans-2-phenylcyclohexanol according to Huynh et al.[20]. The suspension was washed twice with a saturated solution of ammonium chloride and the combined water layers were extracted with ether. The organic layers were dried over $MgSO_4$ and the solvent was evaporated. Distillation at 2 mm Hg yielded 18.2 g (80%) trans-2-phenylcyclohexanol (bp 106-110°C). Recrystallization from pentane resulted in white needles with a melting point of 54.5-55.5 °C (trans-2-phenylcyclohexanol lit. 57-58 °C[20]; 56.5-57 °C[21]). ^{1}H NMR: δ 7.38-7.22 (m, 5H, aromatic); 3.65 (ddd (app as dt), 1H, H1, J=10.0, 9.8, 4.5); 2.41 (ddd, 1H, H2, J=11.6, 10.0, 3.6); 2.14 (m, 1H, H6eq); 1.91-1.22 (m, 7H, H3,4,5 and H6ax); 1.55 (s, 1H, OH). The NMR spectrum is in agreement with the one reported by Whitesell and Lawrence[21].

2-Phenylcyclohexanone (II): 9.5 g (54 mmol) Trans-2-phenylcyclohexanol was oxidized with chromium(VI) oxide and pyridine in methylene chloride following Ratcliffe and Rodehorst[22]. Yield: 9.1 g (52 mmol; 96%) of II. Recrystallization from pentane resulted in white needles with a melting point of 58-59 °C (lit. 61 °C[23]; 58-59 °C[24a]; 57-59 °C[24b]. ^{1}H NMR: δ 7.36-7.11 (m, 5H, aromatic); 3.61 (dd, 1H, H2, J=11.4); 2.55-2.41 (m, 2H, H6); 2.38-1.73 (m, 6H, H3,4,5); IR (KBr): 1695 cm^{-1} (lit. (CCl_4): 1720 cm^{-1} [24b]).

Ethyl 1-hydroxy-2-phenylcyclohexaneacetate (III): 1.65 g (9.5 mmol) 2-Phenylcyclohexanone was alkylated with 1.7 g (10 mmol) ethyl bromoacetate and 0.7 g (10.7 mmol) granular zinc in refluxing benzene following the Reformatsky method described by Cook et al.[25]. Distillation under reduced pressure yielded 2.0 g (7.6 mmol; 80%) ethyl 1-hydroxy-2-phenylcyclohexaneacetate (III) (bp 146-154 °C at 0.8 mm Hg). The configuration was not determined. ^{1}H NMR: δ 7.35-7.21 (m, 5H, aromatic); 3.96 (q, 2H, $C\underline{H}_2CH_3$, J=7.1 Hz); 3.48 (br s, 1H, OH); 2.45 (dd, 1H, H2, J=12.9, 3.6); 2.29 (d, 1H, H1'a, J=13.9); 2.21 (d, 1H, H1'b, J=13.9); 2.08 (m, 1H, H6ax); 1.91-1.28 (m, 7H, H3-H6eq); 1.18 (t, 3H, $CH_2C\underline{H}_3$, J=7.1).

Ethyl 2-phenylcyclohexeneacetate (IV): Dehydration of 2.0 g (7.6 mmol) of III with thionyl chloride (1.1 eq.) and pyridine yielded after distillation at 0.8 mm Hg (bp 123-125 °C) 1.4 g (5.7 mmol; 68%) ethyl 2-phenyl-1-cyclohexeneacetate (IV) and ethyl 2-phenylcyclohexylideneacetate in a ratio of 3 : 1. This mixture was used in the next step.

Ethyl 2-phenylcyclohexeneacetate: ^{1}H NMR: δ 7.38-7.11 (m, 5H, aromatic); 4.11 (q, 2H, $C\underline{H}_2CH_3$, J=7.2); 2.90 (s, 2H, H1'); 2.35-2.08 (m, 4H, H6, H3); 1.81-1.70 (m, 4H, H4, H5); 1.23 (t, 3H, $CH_2C\underline{H}_3$, J=7.2).

Ethyl cis-2-phenylcyclohexaneacetate (V): 2.0 g (8.2 mmol) of IV in 20 ml methanol was hydrogenated by passing hydrogen through the solution at atmospheric pressure, using 0.2 g 5% Pd on carbon as a catalyst. After the reaction was complete (GC), filtration and concentration yielded 1.7 g (6.9 mmol; 84%) of two products (4 : 1 as measured with NMR). This mixture was used as such in the next step.

Major product: ^{1}H NMR: δ 7.31-7.15 (m, 5H, aromatic); 3.96 (q, 2H, $C\underline{H}_2CH_3$, J=7.2); 2.90 (m, 1H, H2); 2.53 (m, 1H, H1); 2.31 (dd, 1H, H1'a, J=15.4, 10.8); 1.95 (dd, 1H, H1'b, J=15.0, 4.1); 2.01-1.33 (m, 8H, H3-H6); 1.16 (t, 3H, $CH_2C\underline{H}_3$, J=7.0).

Cis-2-phenylcyclohexaneethanal (VI): The esters (V) were reduced with DIBALH at -60 °C under dry nitrogen analogously to the method described by Szántay et al.[26]. 4.9 g (20 mmol) esters yielded 2.6 g (13 mmol; 64%) 2-phenylcyclohexaneethanal (VI) (major : minor = 4 : 1 as measured with NMR).

Major product: ^{1}H NMR: δ 9.34 (t, 1H, H2', J=1.5); 7.32-7.15 (m, 5H, aromatic); 2.92 (m, 1H, H2); 2.71-2.05 (m, 3H, H1,H1'); 1.98-1.11 (m, 8H, H3-H6).

Cis-1-allyl-2-phenylcyclohexane (1): 1.0 g (5.0 mmol) of a mixture of aldehydes (VI) was treated with Wittig salt (made from 2.0 g (5.0 mmol) triphenylmethylphosphonium iodide and 3.1 ml 1.6 M BuLi (hexane) in benzene)[27] in THF for eight hours. The resulting orange suspension was filtered and the residue washed with ether. The combined ether layers were washed with water until this was neutral and concentrated after drying over $MgSO_4$. The residue was purified by means of silicagel column chromatography in petroleum ether yielding 0.4 g (2.0 mmol; 40%) 1-allyl-2-phenylcyclohexane (cis/trans = 4 : 1 as measured on GC). The cis and trans isomers were separated by means of preparative gas chromatography (SE 30, T_c = 145°C): 195 mg cis and 47 mg trans isomer (NMR spectrum identical to that of the trans isomer prepared via the other method).

Cis-1-allyl-2-phenylcyclohexane (1, 99% pure): UV (cyclohexane): λ_{max} 260, 254, 233 nm.
^{1}H NMR: δ 7.30-7.25 (m, 2H, meta aromatic); 7.19-7.14 (m, 3H, ortho and para aromatic); 5.51 (m, 1H, H2'); 4.86 (m, 2H, H3'E and H3'Z); 2.90 (dt, 1H, H2, J=11.9, 3.6, 3.6); 2.03 (br ddd, 1H, H1'b, J=12.0, 12.0, 8.4); 2.02-1.35 (m, 10H, H1, H3-H6, H1'a). ^{13}C NMR: δ 145.6 (quat. aromatic); 138.4 (C2'); 128.0/127.7 (ortho and meta aromatic); 125.6 (para aromatic); 115.1 (C3'); 46.3/39.9 (C1, C2); 30.1/28.9/26.5/25.3/20.1 (C3 - C6, C1').
Ethyl 2-phenylcyclohexylideneacetate (VII): First ethyl trimethylsilylacetate was synthesized according to Fessenden and Fessenden[28] in a yield of 59% based on ethyl bromoacetate (lit. 57%, NMR equal to NMR from the literature[28].
Then 9.0 g (52 mmol) 2-phenylcyclohexanone was alkylated with ethyl trimethylsilylacetate and lithium dicyclohexylamide analogous to the method for cyclohexanone described by Shimoji et al.[29] to give predominantly ethyl 2-phenylcyclohexylideneacetate (VII). Purification over silicagel yielded 10.3 g (42 mmol; 81 %) of the ethyl esters of VII and IV in a ratio of 3 : 1 (as measured on GC).
Ethyl 2-phenylcyclohexylideneacetate (VII): ^{1}H NMR: δ 7.38-7.21 (m, 5H, aromatic); 5.91 (s, 1H, H1'); 5.35 (br s, 1H, H2); 4.18 (q, 2H, $C\underline{H}_2CH_3$, J=7.2); 2.52-1.41 (m, 8H, H3-H6); 1.18 (t, 3H, $CH_2C\underline{H}_3$, J=7.2).
Ethyl trans-2-phenylcyclohexaneacetate (VIII): 10.3 g (42 mmol) of VII was hydrogenated analogously to IV in 100 ml methanol at atmospheric pressure. After the reaction was complete (GC), filtration and drying over magnesium sulfate yielded 9.0 g (36.6 mmol; 87%) ethyl 2-phenylcyclohexaneacetate (VIII) (major : minor = 4 : 1 as measured with NMR). The mixture was used as such in the next step.
Major product: ^{1}H NMR: δ 7.33-7.15 (m, 5H, aromatic); 3.98 (q, 2H, $C\underline{H}_2CH_3$; J=7.2); 2.40-1.31 (m, 12H, H1-H6, H1'); 1.16 (t, 3H, $CH_2C\underline{H}_3$, J=7.2).
Trans-2-phenylcyclohexaneethanal (IX): From 9.0 g (36.6 mmol) of a mixture of the ethyl 2-phenyl-cyclohexaneacetates (VIII) was synthesized 1.9 g (9.4 mmol; 26%) 2-phenylcyclohexaneethanal (major (IX) : minor = 3 : 1 as measured with NMR) analogously to the cis isomer. This mixture was used in the next step.
Major product (IX): ^{1}H NMR: δ 9.45 (t, 1H, H2', J=1.4); 7.32-7.09 (m, 5H, aromatic); 2.32-0.82 (m, 12H, H1-H6, H1').
Trans-1-allyl-2-phenylcyclohexane (2): 1.9 g (9.4 mmol) of a mixture of the aldehydes was treated with Wittig salt (made from 4.0 g triphenylmethylphosphonium iodide and 6.3 ml 1.6 M BuLi (hexane) in benzene) analogously to the synthesis of compound **1**. Work-up and purification by means of silicagel chromatography in petroleum ether yielded 0.9 g 1-allyl-2-phenylcyclohexane (4.5 mmol; 48%; trans/cis = 4.5 : 1 as measured on GC). Separation of the isomers by means of preparative gas chromatography resulted in 500 mg trans and 110 mg cis isomer (NMR spectrum identical to the cis isomer prepared via the other method).
Trans-1-allyl-2-phenylcyclohexane (2, 99% pure): UV (cyclohexane): λ_{max} 260, 255, 249 nm. ^{1}H NMR: δ 7.29-7.23 (m, 2H, meta aromatic); 7.19-7.12 (m, 3H, ortho and para aromatic); 5.65 (dddd, 1H, H2', J=16.8, 10.4, 7.8, 6.3); 4.89 (dt, 1H, H3'E, J=10.2, 1.9, 1.9); 4.83 (br d, 1H, H3'Z, J=17.0); 2.23 (dt, H2, J=11.0, 11.0, 3.3); 1.91 (m, 1H, H1'b); 1.6 (m, 1H, H1'a); 2.02-0.98 (m, 9H, H1, H3-H6). ^{13}C NMR: δ 146.4 (quat. aromatic); 137.1 (C2'); 128.3/127.6 (ortho and meta aromatic); 125.8 (para aromatic); 115.6 (C3'); 50.4 (C2); 42.2 (C1); 38.7/36.0/32.0/26.9/ 26.5 (C3-C6, C1').

1-Allyl-2-phenylcyclohexanols (3 and 4)
3.9 g (22 mmol) 2-Phenylcyclohexanone (II) was treated with 0.75 g (31 mmol) magnesium turnings and 3.4 g (28 mmol) allyl bromide in 50 ml THF following the Barbier method[30]. After stirring overnight the mixture was carefully quenched with a saturated solution of ammonium chloride. The water layer was extracted with several portions of ether and the combined ether layers were washed with sodium bicarbonate and brine. Drying over magnesium sulfate and evaporation of the solvent yielded 4.1 g of yellow oil containing 22% of ketone II, 14% of 1-allyl-t-2-phenyl-r-1-cyclohexanol (**3**) and 61% of 1-allyl-c-2-phenyl-r-1-cyclohexanol (**4**) as measured on analytical GC. Separation of the isomers was achieved by silicagel chromatography. The first run in 20% ether in pentane yielded 600 mg (13%) 1-allyl-c-2-phenyl-r-1-cyclohexanol (**4**) and a mixture of the ketone II and 1-allyl-t-2-phenyl-r-1-cyclohexanol (**3**). This mixture was subjected to a second separation in 20% ether in pentane yielding 120 mg (2.5%) 1-allyl-t-2-phenyl-r-1-cyclohexanol (**3**) as a white solid (mp 56-57°C).
1-Allyl-t-2-phenyl-r-1-cyclohexanol (3, 97% pure): UV (cyclohexane): λ_{max} 265, 259, 254 nm. ^{1}H NMR: δ 7.33-7.28 (m, 2H, ortho aromatic); 7.24-7.20 (m, 3H, meta and para aromatic); 5.74 (dddd, 1H, H2', J=17.0, 10.2, 8.5, 5.9); 5.05 (br d, 1H, H3'E, J=10); 4.99 (very br d, 1H, H3'Z, J=17); 2.78 (br dd, 1H, H2, J=12.2, 3.9); 2.50 (dd, 1H, H1'a, J=14.5, 8.5); 1.81 (br dd, H1'b, J=14.5, 5.9); 2.0-1.3 (m, H3-H6). NOE: H2: (ortho aromatic); H2': (H3'E); H1'a: (H1'b/H3'Z). ^{13}C NMR: δ 141.0 (quat. aromatic); 133.7 (C2'); 129.4/128.0 (ortho and meta aromatic); 126.6 (para aromatic); 118.0 (C3'); 73.6 (C1); 54.6 (C2); 37.0/36.7/28.9 (C3, C6, C1'); 26.2/23.2 (C4, C5).
1-Allyl-c-2-phenyl-r-1-cyclohexanol (4, 99.8% pure): UV (cyclohexane): λ_{max} 265, 260, 254 nm. ^{1}H NMR: δ 7.27-7.16 (m, 5H, aromatic); 5.73 (dddd, 1H, H2', J=17.2, 10.0, 7.4, 7.2); 5.03 (br d, 1H, H3'E, J=10.2); 4.93 (ddt, 1H, H3'Z, J=17.0, 2.1, 1, 1); 2.51 (dd, 1H, H2, J=12.9, 3.6); 2.06 (dddd, 1H, H3ax, J=13.1, 13.1, 12.9, 3.5); 2.00 (br dd, 1H, H1'a, J=13.7, 7.4); 1.92 (br dd, 1H, H1'b, J=13.7, 7.2); 1.61 (m, 1H, H3eq); 1.85-1.31 (m, 6H, H4-H6); NOE: H2 (ortho aromatic/ H2'/H1'a/H1'b/H3eq). ^{13}C NMR: δ 142.7 (quat. aromatic); 133.7 (C2'); 129.0/128.0 (ortho and meta aromatic);

126.3 (para aromatic); 118.3 (C3'); 72.2 (C1); 52.0 (C2); 46.4 (C1'); 36.9/29.0 (C3, C6); 26.3/21.5 (C4, C5).
The X-ray structure analysis of **3** was performed by Dr. R.A.G. de Graaff and the result is presented in Figure 13.

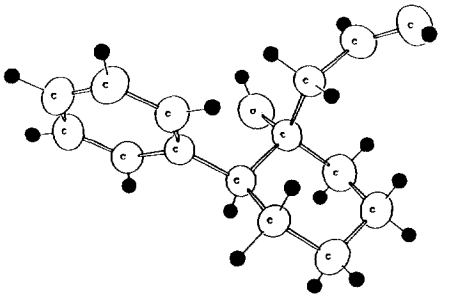


Figure 13 X-ray structure of **3**.

1-Allyl-r-1-methoxy-c-2-phenylcyclohexane (5)

1,1-Dimethoxy-2-phenylcyclohexane (X): A mixture of 30 g of Montmorillonite K-10 clay, 45 ml trimethyl orthoformate and 45 ml methanol was stirred for 15 minutes following the method described by Taylor and Chiang[31]. After filtration of the mixture a moist solid resulted, which was added to a solution of 12.4 g (71 mmol) 2-phenylcyclohexanone (II) in 100 ml pentane. The reaction mixture was stirred for 20 minutes after which the clay was filtered off and washed several times with pentane. Washing of the solution with brine, drying over magnesium sulfate and removal of the solvent yielded 14.6 g (66 mmol; 93%) crude product as a colourless liquid, containing 91% (as measured on GC) of the desired 1,1-dimethoxy-2-phenylcyclohexane (X), which was used without purification in the next step. ^{1}H NMR: δ 7.48-7.11 (m, 5H, aromatic); 3.44 (t, 1H, H2, J=5.1); 3.14 (s, 3H, OCH_3); 2.88 (s, 3H, OCH_3); 2.08-1.50 (m, 8H, H3-H6).

1-Allyl-r-1-methoxy-c-2-phenylcyclohexane (5): To a solution of 5.0 g (22.7 mmol) 1,1-dimethoxy-2-phenylcyclohexane (X) in 150 ml 1,2-dichloroethane under nitrogen was added 12.8 g (57 mmol) zinc bromide which resulted in a pink suspension. After 5 minutes stirring 3.65 ml (23 mmol) allyltrimethylsilane was added dropwise to the solution. Subsequently after one hour stirring at room temperature 25 ml of a saturated solution of sodium bicarbonate was carefully added. Washing of the organic layer with a 5% sodium hydroxide solution (2x), once with a 5% hydrochloric acid solution, extraction of the combined water layers with dichloromethane, washing the dichloromethane with brine, drying over magnesium sulfate and removal of the solvent yielded 4.9 g of crude product. This consisted of 22% of II and 75% of the desired product as measured on GC. 1.50 g of crude product was purified by means of HPLC (eluent: 1% diethyl ether in petroleum ether) resulting in 787 mg (3.4 mmol) of 99.5% pure 1-allyl-r-1-methoxy-c-2-phenylcyclohexane (**5**). UV (cyclohexane): λ_{max} 265, 259, 254 nm. ^{1}H NMR: δ 7.39 (br d, 2H, ortho aromatic); 7.32-7.10 (m, 3H, meta and para aromatic); 5.71 (ddt, 1H, H2', J=17.1, 10.1, 7.4, 7.4); 4.98 (br d, 1H, H3'E, J=10.1); 4.90 (ddt, H3'Z, J=16.8, 2.3, 1.2, 1.2); 3.19 (s, 3H, OCH_3); 2.53 (dd, 1H, H2, J=12.8, 3.5); 2.21 (dd, 1H, H1'a, J=13.6, 7.6); 2.07 (dq, 1H, H3ax, J=12.8, 12.8, 12.8, 3.9); 1.93 (m, 2H, H1'b, H6eq); 1.76 (double m, 1H, H5eq, J=12.9); 1.51 (m, 1H, H3eq); 1.63-1.18 (m, 4H, H4, H5ax, H6ax). NOE: H2': (ortho aromatic/H3'a/H2); H3'a + H3'b: (H2'/H1'a/H1'b); OCH_3: (H1'a/H1'b). ^{13}C NMR: δ 143.1 (quat. aromatic); 134.5 (C2'); 129.8/127.5 (ortho and meta aromatic); 125.9 (para aromatic); 117.4 (C3'); 76.8 (C1); 51.7 (OCH_3); 48.1 (C2); 40.4/30.8/30.2/26.5/21.4 (C3-C6, C1'). MS (EI) m/z (%): M^+-OCH_3 199 (12), 198 (81), 169 (38), 155 (46), 141 (52), 132 (63), 115 (60), 91 (100), 77 (58), 65 (37).

Cis- and trans-1-benzyl-2-vinylcyclohexane (6 and 7)

Trans-2-benzylcyclohexanol (XI): To 3.6 g (0.15 mol) magnesium turnings and 17.4 g (0.14 mol) benzyl chloride in 100 ml THF 12.0 g (0.12 mol) cyclohexene oxide was added at -5° - -10°C[20]. After half an hour the temperature was allowed to rise to room temperature and the mixture was stirred for two hours. After quenching the reaction mixture with ammonium chloride, the water layer was extracted with ether and the organic layers were washed with brine. After drying over $MgSO_4$ and evaporation of the solvent 11.6 g (0.06 mol; 51%) of trans-2-benzylcyclohexanol (XI) remained as a white solid (mp 75-76 °C from hexane; lit. 77 °C[32], 78-79 °C[23]). The NMR was in agreement with the NMR of trans-2-benzylcyclohexanol from the literature[33]. ^{1}H NMR: δ 7.33-7.15 (m, 5H, aromatic); 3.31 (dt, 1H, H1, J=10.4, 10.4, 4.8); 3.17 (dd, 1H, H1''a, J=13.3, 4.0); 2.36 (dd, 1H, H1''b, J=13.3, 8.9); 1.97 (m, 1H, H2); 1.75-0.85 (m, 8H, H3-H6).

2-Benzylcyclohexyl-p-toluenesulfonate (XII): 7.5 g (40 mmol) Trans-2-benzylcyclohexanol (XI) in 14 ml pyridine was cooled to 0°C and 9.5 g (50 mmol) tosyl chloride was added in 15 minutes[34]. After another 15 minutes the mixture was allowed to warm to room temperature and slowly stirred overnight. The mixture was poured into water, which was extracted four times with ether. The combined ether layers were washed with water, dried over $MgSO_4$ and the solvent was evaporated to yield 12.1 g (35 mmol; 88%) of XII (mp 84-85 °C; one isomer as measured with NMR, configuration

not determined). ^{1}H NMR: δ 7.81 (d, 2H, J=8.6, tosyl); 7.32 (d, 2H, J=8.6, tosyl); 7.27-7.02 (m, 5H, phenyl); 4.31 (dt, 1H, H1, J=9.7, 4.3, 4.3); 2.99 (dd, 1H, H1''a, J=13.0, 3.4); 2.43 (s, 3H, CH_3); 2.00 (dd, 1H, H1''b, J=13.4, 10.3); 2.06-0.84 (m, 9H, H2-H6).

2-Benzylcyclohexanecarbonitrile (XIII): 12.1 g (35 mmol) of the tosylate XII was treated with 2.7 g (55 mmol) sodium cyanide in 140 ml dry DMSO at 90°C for 5 hours following Pawson et al.[35]. Yield: 3.6 g (18 mmol; 51%) 2-benzylcyclohexanecarbonitrile (XIII) after distillation at 1.0 mm Hg (bp 132-136°C; configuration not determined). ^{1}H NMR: δ 7.39-7.18 (m, 5H, aromatic); 2.92-2.44 (m, 3H, H1'', H1); 2.09-1.18 (m, 9H, H2-H6).

2-Benzylcyclohexanecarbaldehyde (XIV): To 3.0 g (15 mmol) of XIII was added 22.5 ml 1.0 M DIBALH at -60 °C in dry petroleum ether following Courtin et al.[36]. After stirring for two hours at 0 °C, 30 g silicagel, moistened with 6 ml water and slurried in ether/petroleum ether (1/1), was added slowly and the mixture was stirred at 0 °C for one hour. After drying over $MgSO_4$ and filtering off the solids, the filtrate was extracted with ether. Evaporation of the solvent afforded 2.5 g (12 mmol; 83%) of 2-benzylcyclohexanecarbaldehyde (XIV) (major : minor = 8 : 1 as measured with NMR, H1' of minor: 9.60 (s)), which was subjected at once to the Wittig reaction because of its instability.

Major product: ^{1}H NMR: δ 9.83 (s, 1H, H1'); 7.36-7.15 (m, 5H, aromatic); 2.85-2.28 (m, 3H, H1'', H1); 2.19-1.18 (m, 9H, H2-H6).

Cis- and trans-1-benzyl-2-vinylcyclohexane (6 and 7): Analogously to the synthesis of 1-allyl-2-phenylcyclohexane (**1** and **2**) 1-benzyl-2-vinylcyclohexane was synthesized by the Wittig reaction of 5.05 g (12.5 mmol) $[(C_6H_5)_3P\text{-}CH_3]I$ and 7.8 ml 1.6 M butyllithium with 2.5 g (12.5 mol) 2-benzylcyclohexanecarbaldehyde in THF. After purification by silicagel chromatography (eluent: 1% diethyl ether in petroleum ether) 1.1 g (44%) of 1-benzyl-2-vinylcyclohexane (cis/trans = 6 : 1 as measured on GC) remained as a colourless oil. Separation of the isomers by means of preparative gas chromatography (SE 30 column, 155 °C) yielded 550 mg of the cis isomer (**6**) and 100 mg of the trans isomer (**7**).

Cis-1-benzyl-2-vinylcyclohexane (6, 96% pure): UV (cyclohexane): λ_{max} 269, 261, 255 nm. ^{1}H NMR: δ 7.27-7.22 (m, 2H, meta aromatic); 7.19-7.11 (m, 3H, ortho and para aromatic); 6.09 (ddd, 1H, H1'', J=17.1, 10.4, 8.4); 5.09 (ddd, 1H, H2''E, J=10.5, 2.4, 0.6); 5.02 (ddd, 1H, H2''Z, J=17.1, 2.4, 1.2); 2.55 (dd, 1H, H1'b, J=13.6, 6.2); 2.39 (dd, 1H, H1'a, J=13.6, 8.9); 2.32 (br dq, 1H, H2, J ≈ 8.2, 4.2, 4.2, 4.2); 1.80 (dddt, 1H, H1, J=13.3, 8.9, 6.1, 4.0, 4.0); 1.66 (m, 1H, H5eq or ax); 1.56 (m, 1H, H3eq or ax); 1.55 (m, 1H, H5ax or eq); 1.32 (m, 1H, H6ax); 1.61-1.25 (m, 4H, H3eq or ax, H4 and H6eq). ^{13}C NMR: δ 141.7 (quat. aromatic); 139.8 (C1''); 129.1/128.0 (ortho and meta aromatic); 125.5 (para aromatic); 115.1 (C2''); 43.2/42.0 (C1, C2); 38.7 (C1'); 30.9/27.7/24.8/22.6 (C3-C6).

Trans-1-benzyl-2-vinylcyclohexane (7, 95% pure): UV (cyclohexane): λ_{max} 269, 261, 256 nm. ^{1}H NMR: δ 7.28-7.20 (m, 2H, meta aromatic); 7.18-7.10 (m, 3H, ortho and para aromatic); 5.74 (ddd, 1H, H1'', J=17.1, 10.3, 8.8); 5.05 (dd, 1H, H2''Z, J=17.1, 2.1); 5.03 (dd, 1H, H2''E, J=10.3, 2.1); 3.00 (dd, H1'a, J=13.5, 3.4); 2.08 (dd, 1H, H1'b, J=13.5, 10.3); 1.74 (m, 1H, H2); 1.73 (m, 1H, H4eq); 1.71-1.58 (m, 3H, H3eq, H5eq, H6eq); 1.34 (dtt, 1H, H1, J=11.4, 10.2, 10.2, 3.4, 3.4); 1.25 (m, 1H, H3ax); 1.20 (m, 1H, H4ax); 1.08 (m, 1H, H5ax); 0.85 (dddd, 1H, H6ax, J=14.0, 12.4, 11.4, 4.5). ^{13}C NMR: δ 143.9 (C1''); 141.7 (quat. aromatic); 129.3/127.9 (ortho and meta aromatic); 125.4 (para aromatic); 114.3 (C2''); 48.6/43.5 (C1, C2); 41.0 (C1'); 33.8/31.1/26.1/25.9 (C3-C6).

2-Benzyl-1-vinylcyclohexanols (8 and 9)

2-Benzylcyclohexanone (XV): Trans-2-benzylcyclohexanol (XI) was oxidized with chromium trioxide-pyridine complex analogously to compound I. 4.5 g (24 mmol) Alcohol yielded 4.25 g (23 mmol; 96%) 2-benzylcyclohexanone (XV). ^{1}H NMR: δ 7.35-7.11 (m, 5H, aromatic); 3.22 (dd, 1H, H1''a, J=13, 4); 2.62-2.21 (m, 4H, H2, H1''b, H6); 2.14-1.17 (m, 6H, H3-H5).

IR (liquid film): 1710 cm^{-1} (lit. (CCl_4) 1710 cm^{-1} [37]; (liquid film) 1715 cm^{-1} [38]).

2-Benzyl-1-vinylcyclohexanols (8 and 9): 2-Benzylcyclohexanone (XV) (2.0 g, 11 mmol) was alkylated by means of a Grignard reaction with 13 ml (1.0 M in THF) vinylmagnesium bromide in THF. Usual workup with ammonium chloride and sodium bicarbonate yielded 2.2 g of a yellowish oil still containing 18% ketone and the two isomers of the product in a ratio of 13 : 1 as measured on GC. Separation of the isomers was achieved by silicagel chromatography: first separation in dichloromethane and second separation in 5% ether in petroleum ether yielded 0.8 g c-2-benzyl-1-vinyl-r-1-cyclohexanol (**8**) and 93 mg t-2-benzyl-1-vinyl-r-1-cyclohexanol (**9**).

c-2-Benzyl-1-vinyl-r-1-cyclohexanol (8, 96% pure): ^{1}H NMR: δ 7.27-7.21 (m, 2H, meta aromatic); 7.19-7.09 (m, 3H, ortho and para aromatic); 5.95 (dd, 1H, H1', J=17.3, 10.8); 5.33 (dd, 1H, H2'Z, J=17.3, 1.3); 5.16 (dd, 1H, H2'E, J=10.7, 1.3); 2.91 (dd, 1H, H1''a, J=13.4, 2.4); 2.19 (dd, 1H, H1''b, J=13.4, 10.8); 1.61 (m, 1H, H4eq); 1.53 (m, 1H, H2); 1.50 (m, 1H, H3eq); 1.72-1.38 (m, 4H, H5 + H6); 1.28 (ddt, 1H, H3ax, J=13.1, 11.9, 11.9, 3.4); 1.08 (m, 1H, H4ax). NOE: H1''a: (H1''b/H1'/H2/ortho aromatic); H1': (H2'E/H1''a). ^{13}C NMR: δ 146.0 (C1'); 141.5 (quat. aromatic); 129.1/128.0/125.5 (aromatic); 112.05 (C2'); 74.5 (C1); 46.3 (C2); 39.1 (C6); 36.3 (C1''); 26.0 (C3); 25.6/21.3 (C4, C5).

t-2-Benzyl-1-vinyl-r-1-cyclohexanol (9, 96% pure): ^{1}H NMR: δ 7.28-7.21 (m, 2H, ortho aromatic); 7.18-7.11 (m, 3H, meta and para aromatic); 6.28 (dd, 1H, H1', J=17.3, 10.9); 5.39 (dd, 1H, H2'Z, J=17.3, 1.6); 5.23 (dd, 1H, H2'E, J=10.9, 1.6); 2.99 (dd, 1H, H1''a, J=13.4, 3.6); 2.08 (dd, 1H, H1''b, J=13.4, 10.4); 1.69 (m, 1H, H2); 1.81-1.55 (m, 5H, H6, H5eq,

H4eq, H3eq); 1.45 (m, 1H, H5ax); 1.22-1.04 (m, 2H, H4ax, H3ax). NOE: H1''a: (H1''b/ortho aromatic). ^{13}C NMR: δ 141.4 (quat. aromatic); 140.0 (C1'); 129.2/128.1/125.6 (aromatic); 113.8 (C2'); 75.0 (C1); 49.4 (C2); 40.7 (C6); 36.2 (C1''); 27.9/25.3/23.5 (C3-C5).

Irradiation, purification and characterization

Table 7 Irradiation, detection and isolation conditions

Starting material	Amount irradiated (mg)	Irradiation time (h)	Conversion (%)	T_{col} AGC (°C)	T_{col} PGC (°C)
1	195	9	95	170	175
2	210	7	88	150	145
3	89	8	88	175	
4	225	6	87	145	140
5	500	11	53	155	165
6	250	7	89	150	160
7	100	6	87	150	150
8	300	7.5	93	170	
9	93	6	84	145	

Table 8 Isolation conditions for preparative HPLC and relative retention times (rrt) of the products with respect to the starting material (for compound **8** relative to adduct **8e**).

		rrt of each type of adduct					
comp.	eluent[a]	**ax**	**ay**	**bx**	**by**	**cx**	**cy**
3	A	1.26		1.18			
4	A	1.75		1.46		1.07	1.13
8	B	1.29	1.39		1.11		1.54
9	A	2.83		1.07			

[a] A = 1% 2-methyl-2-butanol/1% diethyl ether in hexane
B = 5% diethyl ether in hexane

Table 9 Meta-adducts (relative retention times on AGC) formed by the irradiation of compounds **1** - **9**.

Compound: meta-adduct: retention time relative to starting material (percentage); other products: (o.p.): retention time relative to starting material (percentage).	
1	**1dy**: 0.95 (7%); **1dx**: 1.02 (16%); **1b**: 1.13 (47%); **1a**: 1.16 (13%); original 2,6 adducts: 1.33 (1%) and 1.52 (1%); o.p.: 0.97 (2%), 1.05 (3%), 1.19 (1%), 1.24 (2%).
2	**2dy**: 0.96 (1%); **2dx**: 0.98 (5%); **2b**: 1.18 (9%); **2a**: 1.21 (11%); **2cx**: 1.28 (34%); **2cy**: 1.37 (22%); o.p.: 1.39 (3%).
3	**3ax** and **3bx**: 1.14 (85%); o.p.: 1.02 (1%), 1.07 (1%).
4	**4dx**: 0.96 (1%); **4ax**: 1.13 (48%); **4bx**: 1.21 (31%); **4cy**: 1.34 (1%); **4cx**: 1.36 (6%).
5	**5dy**: 1.05 (1%); **5ax**: 1.07 (20%); **5bx**: 1.13 (26%); o.p.[a]: 1.23 (2%); 1.26 (2%); 1.35 (2%).
6	**6dy**: 0.85 (4%); **6ax**: 0.95 (24%); **6by**: 1.09 (26%); **6ay**: 1.15 (15%); **6bx**: 1.18 (10%); **6cy**: 1.27 (11%).
7	**7dy**: 0.86 (1%); **7dx**: 0.88 (6%); **7a** and **7b**: 1.05 (23%); **7cx**: 1.15 (40%); **7cy**: 1.24 (12%); o.p.: 1.33 (5%).
8	**8dy**: 0.88 (4%); **8by**: 1.01 (36%); **8ay** and **8e**: 1.04 (47%); **8cy**: 1.26 (1%); o.p.: 0.70 (1%), 0.80 (1%), 1.29 (2%).
9	**9ax**: 0.95 (49%); **9bx**: 0.98 (34%); o.p.: 1.28 (1%).

[a] The original 2,6 adduct has a longer rrt than **5dy** and therefore must be one of the later eluting minor adducts of 2%.

Photoadducts

In this section the systematic names of all adducts will be given. The numbering of the adducts is following the Von Baeyer system from the IUPAC rules[39]. The endo and exo hydrogen atoms are indicated with Ha and Hb, respectively. ^{1}H NMR chemical shifts and coupling constants are presented in Tables 2 - 5.

*Pentacyclo[7.6.0.0^{1,14}.0^{2,7}.0^{11,15}]pentadec-12-ene (**1a**)* (together with **1b** in a ratio of 1 : 1.2): ^{13}C NMR (75.5 MHz): δ 133.1 (C12); 128.6 (C13); 52.9 (C11); 41.5 (C9); 37.9 (C15); other carbon resonances see **1b**.

*Pentacyclo[7.6.0.0^{1,12}.0^{2,7}.0^{11,13}]pentadec-14-ene (**1b**)* (together with **1a** in a ratio of 1.2 : 1): ^{13}C NMR (75.5 MHz): δ 138.0 (C15); 125.4 (C14); 43.0 (C9); 37.2 (C12); other carbon resonances of **1a** and **1b**: CH: 59.7/41.7/40.1/38.2/36.4/32.8/29.8; CH_2: 48.5/38.1/35.1/29.6/28.7/27.4/27.0/24.9/23.5/ 23.2/22.2/21.7; quaternary C's not visible.

*(1RS,2RS,7RS,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-diene (**1dx**)* (91% **1dx** + 7% **1**): ^{13}C NMR (75.5 MHz): δ 133.9 (C13); 133.4 (C12); 131.9 (C14); 130.8 (C15); 64.0 (C10); 42.3 (C9); 41.2/32.2 (C2, C7); 35.0 (C11); 34.0 (C8); 32.8/28.5/26.4/23.0 (C3-C6); quaternary C not visible. MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1543.

*(1RS,2SR,7SR,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-diene (**1dy**)* (96% pure): ^{1}H NMR (300 MHz): NOE: H11b + H10: (H8b). ^{13}C NMR (75.5 MHz): δ 134.7/132.9 (C12, C13); 130.0 (C14); 127.9 (C15); 53.2 (C10); 43.3 (C9); 36.7 (C2); 34.6 (C11); 31.1 (C8); 29.3 (C7); 30.6/26.1/25.8/22.4 (C3-C6); quaternary C not visible. MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1553.

2a and **2b** together in one fraction: too small amount and too impure to measure ^{13}C NMR.

*Pentacyclo[7.6.0.0^{1,14}.0^{2,7}.0^{11,15}]pentadec-12-ene (**2a**)* (together with **2b** in a ratio of 1 : 1.2): MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1557.

*Pentacyclo[7.6.0.0^{1,12}.0^{2,7}.0^{11,13}]pentadec-14-ene (**2b**)* (together with **2a** in a ratio of 1.2 : 1): MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1540.

*(1RS,2SR,7RS,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-diene (**2dx**)* (99% pure): ^{1}H NMR (300 MHz): NOE: H10: (H8b/H7); H2: (H14). ^{13}C NMR (75.5 MHz): δ 135.4 (C14); 133.7 (C15); 133.6* (C12); 133.2* (C13) 62.2 (C1); 49.4 (C10); 44.1 (C2); 41.7 (C7); 39.6 (C9); 33.7 (C11); 33.5 (C8); 30.4 (C3); 34.0/27.4/27.1 (C4-C6). MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1537.

*(1RS,2RS,7SR,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-diene (**2dy**)* (81% **2dy** + 12% **2**): ^{13}C NMR (75.5 MHz): δ 133.4/133.1/129.8/127.8 (C12-C15); 64.0 (C1); 63.2 (C10); 48.8/38.2 (C2, C7); 43.0 (C9); 34.8 (C8 + C11); 32.7/29.7/27.1/27.0 (C3-C6). MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1566.

*(1RS,2SR,7SR,9SR,11SR,14RS,15SR)-Pentacyclo[7.6.0.0^{1,14}.0^{2,7}.0^{11,15}]pentadec-12-en-7-ol (**3ax**):* (97% pure): ^{13}C NMR (100 MHz): δ 133.3 (C12); 128.4 (C13); 52.8 (C11); 47.9 (C10); 47.8 (C2); 42.1 (C8); 39.2 (C9); 37.3 (C14); 37.1 (C15); 36.3 (C6); 29.0/24.5/23.0 (C3/C4/C5); quaternary C's not visible.

MS m/z (%): 216 (13), 198 (72), 183 (8), 169 (14), 155 (20), 150 (100), 137 (20), 132 (40), 120 (56), 117 (38), 108 (15), 92 (9), 91 (47), 77 (26), 69 (13), 67 (9), 57 (18), 55 (17), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found 216.1520.

Eu(FOD)$_3$ complex of **3ax**: ^{1}H NMR (300 MHz): δ 5.87 (H13); 5.72 (H12); 5.4 (H6a); 5.0 (H2 + H8a); 4.65 (H6b); 4.40 (H9), 3.89 (H11); 3.75 (H8b); 3.30 (H15); 3.15 (H5a); 3.1 (H3a); 2.82 (H14); 2.7 (H5b); 2.67 (H10b); 2.5 (H3b + H4a); 2.40 (H10a); 2.32 (H4b).

*(1RS,2SR,7SR,9SR,11SR,12SR,13SR)-Pentacyclo[7.6.0.0^{1,12}.0^{2,7}.0^{11,13}]pentadec-14-en-7-ol (**3bx**):* (96% pure, white solid): ^{1}H NMR (400 MHz): NOE: H15 (H9/H2); H12 (H13/H14); H9(H12): (H2/H15). ^{13}C NMR (100 MHz): δ 137.3 (C15); 126.0 (C14); 56.9 (C9); 51.6 (C2); 47.0 (C8); 36.4 (C12); 35.8 (C10); 32.6 (C13); 29.8 (C11); 27.1/23.1/20.5/17.8 (C3-C6); quaternary C's not visible. MS m/z (%): 216 (3), 198 (23), 183 (12), 175 (90), 170 (8), 155 (26), 142 (10), 141 (20), 130 (19), 117 (34), 115 (23), 104 (14), 92 (12), 91 (100), 79 (11), 67 (4), 65 (7), 55 (11), 51 (4), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found 216.1514.

*(1RS,2RS,7SR,9SR,11SR,14RS,15SR)-Pentacyclo[7.6.0.0^{1,14}.0^{2,7}.0^{11,15}]pentadec-12-en-7-ol (**4ax**):* (99% pure): ^{13}C NMR (75.5 MHz): δ 133.7 (C12); 128.1 (C13); 53.9 (C11); 48.8 (C2); 46.7 (C10); 45.5 (C8); 40.6 (C9); 36.9 (C15); 35.9 (C6); 35.0 (C14); 25.6/22.7/21.1 (C3-C5); quaternary C's not visible. MS m/z (%): 216 (12), 199 (15), 198 (100), 183 (11), 169 (15), 155 (21), 133 (17), 132 (34), 129 (17), 117 (25), 115 (21), 105 (12), 91 (44), 79 (18), 77 (19), 69 (13), 55 (11), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found 216.1510.

Eu(FOD)$_3$ complex of **4ax**: ^{1}H NMR (300 MHz): δ 5.81 (H13); 5.60 (H12); 4.22 (H9); 3.95 (H6eq); 3.81 (H8b); 3.65 (H11); 3.6 (H5ax) 3.2 (H3ax); 2.95 (H2); 2.83 (H14); 2.75 (H6ax); 2.74 (H15); 2.61 (H8a); 2.4 (H4eq); 2.32 (H10b); 2.3 (H3eq); 2.2 (H5eq); 2.08 (H10a); 2.05 (H4ax).

*(1RS,2RS,7SR,9SR,11SR,12SR,13SR)-Pentacyclo[7.6.0.0^{1,12}.0^{2,7}.0^{11,13}]pentadec-14-en-7-ol (**4bx**):* (99% pure): ^{1}H NMR (300 MHz): NOE: H9 (H10a); H12 (H13); H10a (H9/H10b). ^{13}C NMR (75.5 MHz): δ 137.6 (C15); 125.9 (C14); 82.5 (C7); 68.2 (C1); 59.3 (C9); 55.6 (C2); 44.9 (C12); 44.5 (C8); 35.0 (C11); 30.3 (C13); 28.6 (C10); 36.7 (C6); 26.4/22.2/21.0 (C3-C5). MS m/z (%): 216 (2), 198 (17), 183 (6), 175 (100), 169 (7), 155 (18), 141 (10), 129 (17), 117 (19), 115 (17), 105 (13), 91 (47), 78 (9), 77 (13), 69 (21), 55 (13), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found

216.1512.

$Eu(FOD)_3$ complex of **4bx**: ^1H NMR (300 MHz): δ 8.25 (H3ax); 7.74 (H15); 7.05 (H6eq); 6.53 (H8a); 6.07 (H14); 4.96 (H6ax); 4.72 (H8b); 3.99 (H12); 2.76 (H10b); 2.66 (H11); 2.60 (H10a); 2.37 (H13); 6.15/5.5/4.4/4.2/3.4(2H)/3.1 (H2-H5).

*(1RS,2SR,3SR,8RS,10SR,12SR,13RS)-Pentacyclo[8.5.0.0^{2,12}.0^{2,13}.0^{3,8}]pentadec-14-en-8-ol (**4cx**):* (84% + 9% **4**): ^1H NMR (400 MHz): NOE: H11b (H11a/H12). ^{13}C NMR (100 MHz): δ 129.4 (C15); 128.2 (C14); 74.7 (C8); 62.6 (C1); 51.6 (C10); 51.0 (C3); 49.5 (C2); 48.3 (C9); 40.2 (C7); 37.6 (C13); 27.2 (C11); 22.3 (C12); 21.7 (C4); 25.4/21.3 (C5/C6). MS m/z (%): 216 (100), 198 (35), 183 (12), 175 (21), 159 (23), 155 (24), 146 (98), 131 (39), 129 (42), 119 (35), 118 (50), 117 (90), 104 (64), 91 (59), 79 (31), 77 (35), 69 (19), 65 (14), 55 (17), 51 (11), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found 216.1513.

*(1RS,2SR,3RS,8SR,10SR,12SR,13RS)-Pentacyclo[8.5.0.0^{2,12}.0^{2,13}.0^{3,8}]pentadec-14-en-8-ol **4cy**:* (52% **4cy** + 32% **4** + 16% **4cx**): ^{13}C NMR (100 MHz): vinyl CH: 131.4/128.5; sp^3 CH: 55.9/49.6/49.2/40.4/33.8; sp^3 CH_2: 46.6/40.7/30.2/25.72/25.2/21.6. MS m/z (%): 216 (91), 198 (22), 183 (13), 171 (30), 155 (12), 146 (80), 131 (34), 129 (51), 119 (35), 118 (63), 117 (100), 104 (58), 91 (42), 77 (22), 69 (42), 55 (12), exact mass calculated for $C_{15}H_{20}O$ 216.1514, found 216.1518.

*(1RS,2RS,7SR,9SR,10RS)-Tetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-dien-7-ol (**4dx**):* (95% pure): ^{13}C NMR (75.5 MHz): δ 135.0 (C14); 134.4* (C12); 133.0* (C13); 132.1 (C15); 65.4 (C10); 54.4 (C2); 44.9 (C8); 42.5 (C9); 40.5 (C6); 34.9 (C11); 26.5/23.6/21.2 (C3-C5); quaternary C's not visible. MS m/z (%): 216 (100), 198 (33), 186 (13), 181 (47), 171 (19), 155 (21), 146 (71), 131 (35), 129 (43), 119 (42), 118 (81), 117 (82), 104 (54), 91 (58), 79 (22), 77 (32), 69 (54), 55 (20), exact mass calculated for $C_{15}H_{20}O$: 216.1514, found 216.1514.

*(1RS,2RS,7SR,9SR,11SR,14RS,15SR)-7-Methoxypentacyclo[7.6.0.0^{1,14}.0^{2,7}.0^{11,15}]pentadec-12-ene (**5ax**)* (47% **5ax**, 20% **5dy**, 24% **5**).

*(1RS,2RS,7SR,9SR,11SR,12SR,13SR)-7-Methoxypentacyclo[7.6.0.0^{1,12}.0^{2,7}.0^{11,13}]pentadec-14-ene (**5bx**)* (68% **5bx**; 10% **5**, 14% **5ax**): ^1H NMR (300 MHz): NOE: OCH_3: (H8a).

*(1RS,2SR,7RS,9SR,10RS)-7-Methoxytetracyclo[7.4.2.0^{1,10}.0^{2,7}]pentadeca-12,14-diene (**5dy**)* (20% **5dy**, 47% **5ax**, 24% **5**).

*(1RS,3SR,8SR,9RS,11RS,14SR,15RS)-Pentacyclo[7.6.0.0^{1,14}.0^{3,8}.0^{11,15}]pentadec-12-ene (**6ax**)* (88% **6ax** + 6% **6dy**): ^{13}C NMR (75.5 MHz): δ 133.0 (C12); 129.0 (C13); 51.1 (C11); 47.6 (C10); 45.9 (C9); 44.5 (C8); 42.2 (C15); 39.4 (C3); 36.4 (C14); 34.8 (C2); 28.8/27.7/24.8/22.9 (C4-C7); quaternary C not visible. MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1548.

*(1RS,3RS,8RS,9RS,11RS,14SR,15RS)-Pentacyclo[7.6.0.0^{1,14}.0^{3,8}.0^{11,15}]pentadec-12-ene (**6ay**).*

*(1RS,3RS,8RS,9RS,11RS,12RS,13RS)-Pentacyclo[7.6.0.0^{1,12}.0^{3,8}.0^{11,13}]pentadec-14-ene (**6bx**)* (94% pure): MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1558.

*(1RS,3SR,8SR,9Rs,11RS,12RS,13RS)-Pentacyclo[7.6.0.0^{1,12}.0^{3,8}.0^{11,13}]pentadec-14-ene (**6by**)* (83% **6by** + 8% **6ay**): ^1H NMR (300 MHz): NOE: H14 + H15: (H13 + H2a); H9 + H3: (H8, H2a, H2b, H10a). ^{13}C NMR (100 MHz): δ 140.5 (C15); 124.4 (C14); 66.4 (C9); 66.2 (C1); 46.1 (C12); 43.0 (C8); 42.9 (C3); 36.2 (C2); 34.5 (C11); 33.6 (C13); 27.0/25.9/23.2/21.2/24.6 (C4-C7, C10). MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1551.

*(1RS,3RS,8RS,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{3,8}]pentadeca-12,14-diene (**6dy**)* (99% pure): ^{13}C NMR (75.5 MHz): δ 135.9* (C13); 133.0* (C12); 129.0 (C15); 128.7 (C14); 61.0 (C1); 54.8 (C10); 48.7 (C9); 36.7 (C8); 34.6 (C11); 33.6 (C2); 29.8 (C3); 31.1/28.7/26.7/22.6 (C4-C7). MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1529.

*Pentacyclo[7.6.0.0^{1,14}.0^{3,8}.0^{11,15}]pentadec-12-ene (**7a**)* (together with **7b** in a ratio of 1 : 4, next to 17% **7dx** and 6% **7dy**): MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1550.

*Pentacyclo[7.6.0.0^{1,12}.0^{3,8}.0^{11,13}]pentadec-14-ene (**7b**)* (together with **7a** in a ratio of 4 : 1, next to 17% **7dx** and 6% **7dy**): ^{13}C NMR (50 MHz): δ 138.3 (C15); 124.6 (C14); 66.8 (C9); 49.0/48.2/45.4 (C3/C8/C12); 32.9/31.1 (C11/C13); 38.8/32.7/28.5/26.7/26.3/25.0 (C2, C4-C7, C10); quaternary C not visible. MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1554.

*(1RS,3SR,8RS,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{3,8}]pentadeca-12,14-diene (**7dx**)* (isolated with 22% **7dy**): ^{13}C NMR (75.5 MHz): δ 136.6 (C13); 135.1 (C15); 133.6 (C14); 133.1 (C12); 49.8 (C10); 46.6 (C9); 45.8 (C8); 41.6 (C3); 34.1 (C2); 33.7 (C11); 35.2/34.5/27.6/27/1 (C4-C7). MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1540.

*(1RS,3RS,8SR,9RS,10SR)-Tetracyclo[7.4.2.0^{1,10}.0^{3,8}]pentadeca-12,14-diene (**7dy**)* (isolated with 78% **7dx**): ^{13}C NMR (75.5 MHz): δ 135.7* (C13); 133.0* (C12); 130.4 (C14); 127.4 (C15); 63.1 (C10); 48.6 (C9); 47.2/38.6 (C3/C8); 36.5/34.7/33.3/32.9/27.2/26.9 (C2, C4-C7, C11); quaternary C not visible. MS: Exact mass calculated for $C_{15}H_{20}$ 200.1565, found 200.1546.

*(1RS,3RS,8RS,9SR,11RS,14SR,15RS)-Pentacyclo[7.6.0.0^{1,14}.0^{3,8}.0^{11,15}]pentadec-12-en-8-ol (**8ay**)* (97% pure): ^{13}C NMR (75.5 MHz): δ 134.3 (C12); 127.6 (C13); 53.6 (C11); 53.0 (C9); 51.0 (C3); 39.7 (C15); 38.3 (C14); 36.8 (C10); 34.9 (C2); 36.2/25.8/25.6/21.5 (C4-C7); quaternary C's not visible. MS (CI/NH_3) m/z (%): 234 $[M + NH_4]^+$ (29), 217 $[M + H]^+$ (26), 199 (45), 149 (94), 107 (100).

*(1RS,3RS,8RS,9SR,11RS,12RS,13RS)-Pentacyclo[7.6.0.0^{1,12}.0^{3,8}.0^{11,13}]pentadec-14-en-8-ol (**8by**)* (98% pure, white

solid, mp 68 - 69°C): ^{1}H NMR (300 MHz): NOE: H12: (H2b); H9 + H10b + H2a: (H15, H7ax). ^{13}C NMR (75.5 MHz): δ 139.6 (C15); 125.0 (C14); 70.1 (C9); 51.4 (C3); 44.7 (C12); 36.9 (C2); 34.8 (C7); 34.6 (C11); 33.4 (C13); 23.0 (C10); 25.84/25.78/21.0 (C4-C6); quaternary C's not visible. MS (CI/NH_3) m/z (%): 234 $[M + NH_4]^+$ (97), 217 $[M + H]^+$ (100), 199 (94).

*(1RS,2RS,4SR,9SR,10SR,12RS,13SR)-Pentacyclo[8.5.0.0^{2,12}.0^{2,13}.0^{4,9}]pentadec-14-en-9-ol (**8cy**)* (45% **8cy**, 37% **8**, 16% unknown compound (rrt 1.29)): ^{13}C NMR (100 MHz): δ 130.9 (C15); 129.2 (C14); 65.3 (C10); 54.0 (C1); 47.4 (C4); 44.9 (C13); 35.5 (C3); 27.1 (C12); 24.0 (C11); 36.8/29.7/26.4/21.5 (C5-C8). MS (CI/NH_3) m/z (%): 234 $[M + NH_4]^+$ (100), 217 $[M + H]^+$ (86), 199 (96), 107 (23).

*Pentacyclo[8.5.0.0^{2,12}.0^{2,15}.0^{4,9}]pentadec-13-en-9-ol (**8e**)* (GC: 99% pure; NMR: 25% contamination of an unknown compound): ^{1}H NMR (300 MHz): δ 5.56 (dd, H14, J=5.4, 2.2); 5.39 (dd, H13, J=5.4, 2.5); 2.78 (dd, H12, J=6.6, 2.5); 2.42 (m, H4); 2.35 (m, H10); 2.26 (dd, H3a*, J=14.8, 5.1); 1.88 (m, H11b); 1.62 (br d, H15, J=7); 1.50 (dd, H3b*, J=14.8, 7.8); 1.46 (m, H1); 2.5-1.3 (H5-H8, H11a). ^{13}C NMR (75.5 MHz): δ 132.8 (C13); 127.6 (C14); 53.1 (C12); 50.0 (C4); 42.0 (C10); 36.7 (C15); 39.9 (C11); 34.4 (C1); 34.3/32.6/28.1/24.9/22.7 (C3, C5-C8); quaternary C not visible. MS (CI/NH_3) m/z (%): 234 $[M + NH_4]^+$ (100), 217 $[M + H]^+$ (97), 107 (29).

*(1RS,3SR,8RS,9SR,11RS,14SR,15RS)-Pentacyclo[7.6.0.0^{1,14}.0^{3,8}.0^{11,15}]pentadec-12-en-8-ol (**9ax**)* (97% pure): ^{13}C NMR (100 MHz): δ 133.2 (C12); 128.5 (C13); 51.0 (C11); 49.2 (C9); 46.8 (C3); 42.1 (C15); 41.1 (C10); 36.5 (C14); 34.0 (C2); 36.0/25.9/22.5/22.4 (C4-C7); quaternary C's not visible.

*(1RS,3SR,8RS,9SR,11RS,12RS,13RS)-Pentacyclo[7.6.0.0^{1,12}.0^{3,8}.0^{11,13}]pentdec-14-en-8-ol (**9bx**)* (92% pure): ^{1}H NMR (300 MHz): NOE: H15: (H9, H2a); H12 + H9: (H2b, H15). ^{13}C NMR (100 MHz): δ 140.0 (C15); 125.2 (C14); 62.7 (C9); 51.0 (C3); 45.2 (C12); 38.8 (C2); 34.3 (C13); 33.4 (C11); 23.4 (C10); 33.1/33.0/25.4/23.0 (C4-C7); quaternary C's not visible.

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REFERENCES AND NOTES

1. Wender, P.A.; Siggel, L.; and Nuss, J.M., *Organic Photochemistry*, Padwa, E., Ed., Marcel Dekker, New York, 1989, Vol. 10, Chapter 4, p. 357.
2. Cornelisse, J., *Chem. Rev.*, **1993**, *93*, 615.
3. a. Wender, P.A. and Dreyer, G.B., *Tetrahedron*, **1981**, *37*, 4445.
   b. Wender, P.A. and DeLong, M.A., *Tetrahedron Lett.*, **1990**, *31*, 5429.
   c. Wender, P.A.; Ternansky, R.; DeLong, M.; Singh, S.; Olivero, A. and Rice, K., *Pure Appl. Chem.*, **1990**, *62*, 1597.
4. Gilbert, A. and Taylor, G.N., *J. Chem. Soc., Perkin Trans. I*, **1980**, 1761.
5. De Zwart, E.W., De Haan, R. and Cornelisse, J., *J. Photochem. Photobiol. A: Chem.*, **1994**, *77*, 161.
6. Blakemore, D.C. and Gilbert, A., *J. Chem. Soc., Perkin Trans. I*, **1992**, 2265.
7. Ellis-Davies, G.C.R.; Gilbert, A.; Heath, P.; Lane, J.C.; Warrington, J.V. and Westover, D.L., *J. Chem. Soc., Perkin Trans. II*, **1984**, 1833.
8. Bryce-Smith, D.; Drew, M.G.B.; Fenton, G.A.; Gilbert, A. and Proctor, A.D., *J. Chem. Soc., Perkin Trans. II*, **1991**, 779.
9. Ellis-Davies, G.C.R.; Cornelisse, J.; Gilbert, A. and Kashoulis-Koupparis, A., *Tetrahedron Lett.*, **1988**, *29*, 4319.
10. Zhang, C.; Bourgin, D. and Keese, R., *Tetrahedron*, **1991**, *47*, 3059 and references therein.
11. Wender, P.A.; Von Geldren, T.W. and Levine, B.H., *J. Am. Chem. Soc.*, **1988**, *110*, 4858.
12. Pallmer, M. and Morrison, H., *J. Org. Chem.*, **1980**, *45*, 798.

13. The second letter, **x** or **y**, denotes the stereochemistry of the cyclohexane ring fusion: **x** when the substituent on the β-carbon atom is endo, **y** when it is exo. When two substituents are present on the β-carbon atom, the structure is indicated with **x** if the oxygen-containing substituent is endo.
14. Srinivasan, R., *J. Am. Chem. Soc.*, **1971**, *93*, 3555.
15. Gorter, S.; Barentsen, H.M. and Cornelisse, J., to be published.
16. a. De Vaal, P.; Osselton, E.M.; Krijnen, E.S.; Lodder, G. and Cornelisse, J., *Recl. Trav. Chim. Pays-Bas*, **1988**, *107*, 407 and references therein.
b. Jans, A.W.H.; Lugtenburg, J.; Kruk, C. and Cornelisse, J., *Org. Magn. Reson.*, **1982**, *19*, 58.
c. Jans, A.W.H.; Van Arkel, B.; Osselton, E.M. and Cornelisse, J., *Magn. Reson. Chem.*, **1985**, *23*, 540 and references therein.
17. Mani, J.; Cho, J.-H.; Astik, R.B.; Stamm, E.; Bigler, P.; Meyer, V. and Keese, R., *Helv. Chim. Acta*, **1984**, *67*, 1930.
18. a. Neijenesch, H.A.; Ridderikhoff, E.J.; Ramsteijn, C.A. and Cornelisse, J., *J. Photochem. Photobiol. A: Chem.*, **1989**, *48*, 317.
b. Neijenesch, H.A.; de Ruiter, R.J.P.J.; Ridderikhoff, E.J.; Van den Ende, J.O.; Laarhoven, L.J.; Van Putten, L.J.W. and Cornelisse, J., *J. Photochem. Photobiol. A: Chem.*, **1991**, *60*, 325.
19. a. Conformer with lowest heat of formation calculated with MM2 and calculation of the coupling constants on the basis of reference 19b implemented in the program Model (version KS2.96) provided by the CAOS/CAMM Center from the Catholic University Nijmegen.
b. Haasnoot, C.A.G.; De Leeuw, F.A.A.M. and Altona, C., *Tetrahedron*, **1980**, *36*, 2783.
20. Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G., *Tetrahedron Lett.*, **1979**, *17*, 1503.
21. Whitesell, J.K. and Lawrence, R.M., *Chimia*, **1986**, *40*, 318.
22. Ratcliffe, R. and Rodehorst, R., *J. Org. Chem.*, **1970**, *35*, 4000.
23. Cornubert, R.; Barraud, G.; Cormier, M.; Descharmes, M. and Gunther Eggert, H., *Bull. Soc. Chim. Fr.*, **1955**, 400.
24. a. Backmann, W.E. and Fornefeld, E.J., *J. Am. Chem. Soc.*, **1950**, *72*, 5529.
b. House, H.O.; Phillips, W.V.; Sayer, T.S.B. and Yau, C.-C., *J. Org Chem.*, **1978**, *43*, 700.
25. Cook, J.W.; Hewett, C.C and Lawrence, C.A., *J. Chem. Soc.*, **1936**, 71.
26. Szántay, C.; Töke, L. and Kolonits, P., *J. Org. Chem.*, **1966**, *31*, 1447.
27. Wittig, G. and Schoellkopf, U., *Org. Syntheses*, **1960**, *40*, 66.
28. Fessenden, R.J. and Fessenden, J.S., *J. Org. Chem.*, **1967**, *32*, 3535.
29. Shimoji, K.; Taguchi, H.; Oshima, K.; Yamamoto, H. and Nozaki, H., *J. Am. Chem. Soc.*, **1974**, *96*, 1620.
30. Dreyfuss, M.P., *J. Org. Chem.*, **1963**, *28*, 3269.
31. Taylor, E.C. and Chiang, C., *Synthesis*, **1977**, 467.
32. Moreau, M.; Quagliaro, R.; Longeray, R. and Dreux, J., *Bull. Soc. Chim. Fr.*, **1969**, 1362.
33. Narasaka, K.; Kusama, H. and Hayashi, Y., *Tetrahedron*, **1992**, *48*, 2059.
34. Tipson, R.S., *J. Org. Chem.*, **1944**, *9*, 235.
35. Pawson, B.A.; Cheung, H.C.; Gurbaxani, S. and Sanay, G., *J. Am. Chem. Soc.*, **1970**, *92*, 336.
36. Courtin, J.M.L.; 'T Lam, G.K.; Peters, A.J.M. and Lugtenburg, J., *Recl. Trav. Chim. Pays-Bas*, **1985**, *104*, 281.
37. House, H.O.; Gall, M. and Olmstead, H.D., *J. Org. Chem.*, **1971**, *36*, 2361.

38. Hegedus, L.S.; Williams, R.E.; Mc Guire, M.A. and Hayashi, T., *J. Am. Chem. Soc.*, **1980**, *102*, 4973.
39. IUPAC, *Nomenclature of Organic Chemistry*, Sections A,B,C,D,E,F and H, 4th ed., Pergamon Press, Oxford, 1979.

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