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Intramolecular *Meta* Photocycloaddition of Conformationally Restrained 5-Phenylpent-1-enes. Part II: Steric and Electronic Effects caused by 4-Mono- and 4-Disubstitution

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Abstract: The meta photocycloaddition of 4-substituted 5-phenylpent-1-enes, **10** - **18**, has been studied. The monosubstituted derivatives always prefer 2,6 addition, independent of the size of the substituent. For 2,6 addition two basic conformations are possible. Disubstituted compounds yield predominantly 1,3 addition with the sterically more demanding group exo. Except for the methoxymethyl and THF derivative the oxygen is found exo as a result of repulsion, while the monohydroxy derivative gives also endo which might be explained by hydrogen bonding. The products from compound **11** change from mainly endo-OH in cyclohexane to chiefly exo-OH in methanol. Much similarity is found with Diels-Alder cycloaddition.

INTRODUCTION

In our preceding article[1] we have reported the results of the intramolecular meta photocycloaddition of the cycloalkane derivatives **1** - **9** of 5-phenylpent-1-ene depicted in Figure 1. The most striking phenomenon resulting from their irradiation was that for 2,6 addition two conformations seemed to be possible, while for 1,3 addition only one conformation gave adducts, except for **6**. Most results could be explained on the basis of steric considerations. The hydroxylated derivatives **4**, **8** and **9**, however, showed some preferences not expected

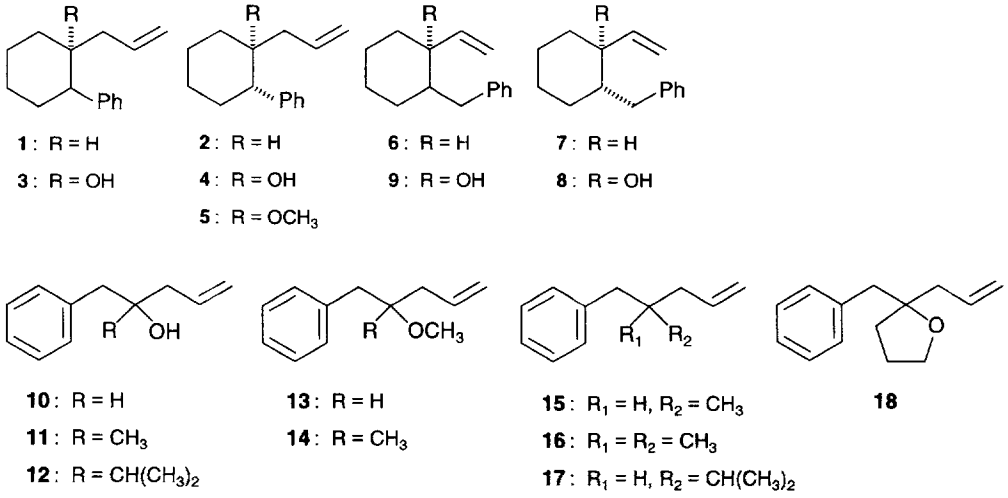


Figure 1 Derivatives of 5-phenylpent-1-ene.

on the basis of steric considerations, compared to their alkane analogues. The major 2,6 adduct of compound **4** has β-OH endo (see Figure 2 for endo/exo), while the 2,6 adduct with β-H endo of compound **2** is the minor product. Similarly compound **5** yields only the 2,6 adduct with the methoxy group exo in accordance with steric demands. From compound **8** only 1,3 adducts with exo OH were isolated, while sterically the other mode of addition with endo OH was expected. Moreover, this compound yielded a product, which was tentatively identified as the unusual 2,6 adduct with 1,5 cyclopropane ring closure. For 1,3 addition of compound **9** both configurations of the OH group would be expected on the basis of steric considerations, while only one is found with OH exo. In all these cases the OH group must have been close to the benzene ring or to the alkene during the addition. In these compounds the OH or OCH_3 is attached to the β- or γ-carbon atom of the chain. We chose to investigate the β-position thoroughly, also because only one substituted 5-phenylpent-1-ene has been reported in the literature[2].

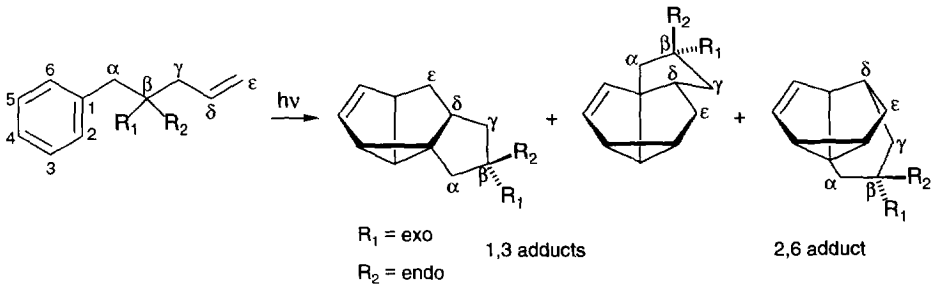


Figure 2 Intramolecular meta photocycloaddition of 4,4-R_1,R_2-5-phenylpent-1-enes. Endo/exo designation of substituents on the connecting chain in the adducts.

We have synthesized and irradiated compounds **10** - **12** (Figure 1) to study the effect of the OH group. To differentiate between an effect induced by the proton or the oxygen atom of the OH group, two compounds with a β-methoxy group, **13** and **14**, were investigated. For comparison the β-alkyl derivatives, **15** - **17**, were studied as well as the cyclic ether **18**.

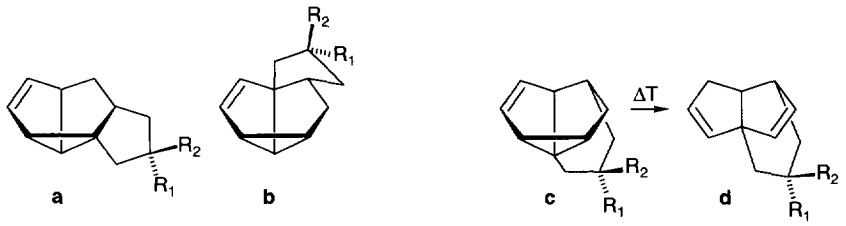
RESULTS AND DISCUSSION

Irradiation, isolation and characterization

Compounds **10** - **18** were irradiated in cyclohexane (1% w/v) and the products[3] isolated (Figure 3). The photoproducts were identified by means of NMR. 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 configurations of the 1,3 adducts of compound **11** were also determined by additional $Eu(FOD)_3$ experiments and - for adducts of type **b** - by NOE measurements on their trimethylsilyl derivatives; these structures have served as references for the other compounds. The ^{1}H NMR chemical shifts and coupling constants are presented in Tables 1a-d.

2,6 versus 1,3 addition

The ratios of 2,6 : 1,3 addition are presented in Table 2. The results for the parent compound 5-phenylpent-1-ene (**P**) have been included. 4-Methyl-5-phenylpent-1-ene (**15**) has been studied by Gilbert and



10ax (6%)			**10cx** (21%)	R_1 = H, R_2 = OH
10ay (15%)	**10by** (12%)		**10cy** (23%)	R_1 = OH, R_2 = H
11ax (35%)	**11bx** (27%)		**11cx** (7%)	R_1 = CH_3, R_2 = OH
11ay (13%)	**11by** (6%)			R_1 = OH, R_2 = CH_3
12ax (41%)	**12bx** (42%)			R_1 = $CH(CH_3)_2$, R_2 = OH
			13cx (22%)	R_1 = H, R_2 = OCH_3
13ay (14%)	**13by** (16%)		**13cy** (30%)	R_1 = OCH_3, R_2 = H
14ax (5%)	**14bx** (13%)			R_1 = CH_3, R_2 = OCH_3
14ay (35%)	**14by** (26%)			R_1 = OCH_3, R_2 = CH_3
15a +	**15b** (20%)	R_1/ R_2 = H, CH_3	**15dx** (38 or 34%)	R_1 = H, R_2 = CH_3
			15dy (33 or 37%)	R_1 = CH_3, R_2 = H
16a (32%)	**16b** (37%)			R_1 = R_2 = CH_3
17a +	**17b** (<26%)	R_1/ R_2 = H, $CH(CH_3)_2$	**17dx** (29%)	R_1 = H, R_2 = $CH(CH_3)_2$
			17dy (24%)	R_1 = $CH(CH_3)_2$, R_2 = H
18ax (6%)	**18bx** (11%)		**18cx** (7%)	R_1 - R_2 = -$CH_2CH_2CH_2O$-
18ay (28%)	**18by** (18%)		**18cy** (3%)	R_1 - R_2 = -$OCH_2CH_2CH_2$-

Figure 3 Irradiation products (yield determined by AGC at the end of the reaction); for 2,6 adducts the combined yields of primary and rearranged adducts are given.

coworkers[2]. These authors have reported the photochemical formation of two 2,6 adducts from this compound. In addition, however, there was a considerable amount of unidentified material which may have contained products from 1,3 photocycloaddition. The mono substituted compounds, **10**, **13**, **15** and **17** still give predominantly 2,6 addition like the parent compound **P** due to the stabilizing effect of the alkyl chain[4]. The disubstituted compounds, **11**, **12**, **14**, **16** and **18** all add predominantly in the 1,3 mode implying that the introduction of a second substituent on the β-carbon seriously hampers the molecule to adopt the geometry necessary for 2,6 addition and thus overrules the electronic stabilizing effect.

In the literature this disubstitution effect on intramolecular reactions is known as the gem-dialkyl effect. This gem-dialkyl effect has been explained in several ways[5]: i. by the number of gauche interactions produced during cyclization; ii. Thorpe-Ingold effect: substitution of both hydrogens on a carbon atom compresses the internal angle of the carbon chain; iii. (mostly adopted) favourable rotamer distribution for cyclization. Sternbach and co-workers[6a] have published work on the intramolecular Diels-Alder reaction of α-(1,1-R_1,R_2-3-butenyl)-2-furanmethanols (Figure 4), which also have three carbon atoms between the reacting groups. The conformation necessary for cyclization is very similar to our 1,3 addition. They found that the β-carbon atom had to be disubstituted to induce cyclization with R = dithiane, SEt, OEt, Pr, but two methyl groups were too small to induce cyclization. In 1988 Cauwberghs et al.[5] reported that introduction of one t-butyl group at the

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

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
10ax	H	OH	2.19	1.99	5.63	5.39	3.12	-	-	-	-	-	4.47	-	-	2.4-1.6
10ay	OH	H	2.39	1.94	5.64	5.40	3.22	1.87	1.97	2.21	2.10	1.55	4.45	2.01	1.59	
11ax	CH_3	OH	2.27	1.93	5.64	5.41	3.21	1.77	1.75	2.43	1.51	2.04		1.72	1.85	1.43 (s, CH_3)
11ay	OH	CH_3	2.40	1.91	5.64	5.40	3.21	1.85	2.00	2.27	1.94	1.60		1.92	1.56	1.35 (s, CH_3)
12ax	iPr	OH	2.24	1.95	5.65	5.44	3.25	1.81	1.69	2.52	1.41*	2.01*		1.94$^+$	1.60$^+$	1.75 (sept, C<u>H</u>(CH_3)$_2$, J=6.9); 0.95 and 0.93 (d, CH_3, J=6.9)
13ay	OCH_3	H	2.33	1.92	5.63	5.40	3.19	1.80	1.89	2.15	2.03	1.60	3.94	1.90	1.69	3.30 (s, OCH_3)
14ax	CH_3	OCH_3	2.27	1.92	5.64	5.40	3.22	1.8 -	1.7	2.35	2.16*	1.42*		1.96$^+$	1.56$^+$	3.22 (s, OCH_3); 1.38 (s, CH_3)
14ay	OCH_3	CH_3	2.32	1.88	5.62	5.40	3.17	1.75	1.94	2.20	1.80	1.69		1.68	1.82	3.21 (s, OCH_3); 1.27 (s, CH_3)
15a	CH_3[c]		2.23	1.88	5.61	5.40	3.22	-	1.75	2.23	-	-	2.22	-	-	2.2-1.6 and 1.42-1.22; 1.05 (d, CH_3, J=6.7)
16a	CH_3	CH_3	2.26	1.87	5.63	5.39	3.21	1.76	1.82	2.31	1.73	1.27		1.55*	1.41*	1.13 and 1.02 (s, CH_3)
17a	iPr[c]		2.21	1.88	5.60	5.41	3.23	-	1.71	-	-	-	-	-	-	2.3-1.2; 0.86 (d, both CH_3, J=6.6)
18ax	-$CH_2CH_2CH_2O$-		2.26	1.93	5.64	5.40	3.16	1.83 -	1.70	2.36	2.16*	1.48*		1.94$^+$	1.54$^+$	3.79 (br t, H5', J=6.6); 2.01-1.80 (m, H3', H4')
18ay	-$OCH_2CH_2CH_2$-		2.38	1.89	5.63	5.40	3.19	1.78	1.97	2.20	1.91	1.66		1.80	1.67	3.82 (m, H5'); 1.93-1.78 (m,H3', H4')

adduct	R_1	R_2	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 J
10ax	H	OH	6.9	6.5	2.2	5.4	2.3	-	-	-	-	-	6.9	6.9	6.9	6.9	
10ay	OH	H	6.5	5.6	2.2	5.4	2.4	5.2	6.3	9.2	9.0	3.2	4.9	3.3	4.9	3.3	b,e=+; c,e=+; i_b,k_b=1.7
11ax	CH_3	OH	6.4	5.7	2.2	5.4	2.5	4.7	6.4	9.1	6.4	9.1					
11ay	OH	CH_3	6.2	5.8	2.2	5.4	2.5	5.3	6.7	9.5	9.5	3.1					i_b,k_b=1.8
12ax	iPr	OH	6.2	5.6	2.2	5.3	2.5	5.2	6.4	9.2	9.5	7.8					h,k_a=+;i_b,k_b=2.5
13ay	OCH_3	H	6.0	5.6	2.3	5.4	2.3	5.2	6.4	9.1	8.9	4.3	4.8	4.2	5.5	4.0	b,e=+; c,e=+; i_b,k_b=1.4
14ax	CH_3	OCH_3	6.2	5.9	2.2	5.3	2.4	-	6.9	8.8	9.3	5.0					
14ay	OCH_3	CH_3	6.1	5.7	2.3	5.4	2.4	5.2	6.4	9.3	8.8	4.8					i_b,k_b=1.7
15a	CH_3[c]		6.5	5.9	2.2	5.4	2.4	-	-	-	-	-	-	-	-	-	
16a	CH_3	CH_3	6.4	5.3	2.2	5.4	2.4	5.3	6.8	9.0	9.0	5.7					
17a	iPr[c]		6.4	5.6	2.3	5.3	2.5	5.2	-	-	-	-	-	-	-	-	
18ax	-$CH_2CH_2CH_2O$-		6.2	5.9	2.2	5.4	2.4	-	6.6	9.4	9.4	4.2					
18ay	-$OCH_2CH_2CH_2$-		6.5	5.6	2.3	5.4	2.4	5.2	6.4	9.4	9.0	3.8					b,e=+; c,e=+; i_b,k_b=1.5

Table 1b 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **b**.[a,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
10by	OH	H	1.74	2.49	1.84	5.53	5.32	2.05	1.75 - 1.65		2.07*	1.65*	4.36	2.25	1.76	
11bx	CH_3	OH	1.69	2.25	1.80	5.51	5.43	2.47	1.8 - 1.6		1.64	1.8-1.6		2.00	2.00	1.42 (s, CH_3)
11by	OH	CH_3	1.75-1.7	2.52	1.84	5.53	5.32	2.09	1.75 - 1.7		1.77	1.91		1.94	2.02	1.32 (s, CH_3)
12bx	iPr	OH	1.69	2.23	1.79	5.51	5.45	2.47	1.80 - 1.65		1.53	1.72		1.81	2.06	1.72 (sept, C<u>H</u>$(CH_3)_2$, J=6.8); 0.97 and 0.95 (d, CH_3, J=6.8)
13by	OCH_3	H	1.72	2.46	1.83	5.53	5.32	1.97	1.75 - 1.6		2.05	1.66	3.86	2.13	1.84	3.31 (s, OCH_3)
14bx	CH_3	OCH_3	1.68	2.27	1.80	5.51	5.41	2.33	1.8 - 1.7		1.89	1.54		2.10	1.83	3.15 (s, OCH_3); 1.35 (s, CH_3)
14by	OCH_3	CH_3	1.74	2.48	1.82	5.52	5.32	2.08	1.85 - 1.7		1.63	1.98		1.75	2.13	3.26 (s, OCH_3); 1.24 (s, CH_3)
15b	CH_3[c]		1.66	2.26	1.79	5.48	5.36	-	-	-	-	-	2.06	-	-	2.2-1.6 and 1.42-1.22; 1.06 (d, CH_3, J=6.5)
16b	CH_3	CH_3	1.67	2.30	1.78	5.49	5.35	2.22	1.7 - 1.65		1.37	1.59		1.71*	1.64*	1.15 and 0.95 (s, CH_3)
17b	iPr[c]		1.66	2.24	1.78	5.49	5.36	-	-	-	-	-	1.66	1.99*	1.50*	2.3-1.2; 1.49 (m, C<u>H</u>$(CH_3)_2$); 0.89 (d, both CH_3, J=6.5)
18bx	-$CH_2CH_2CH_2O$-		1.68	2.26	1.81	5.52	5.42	2.35	1.8 - 1.65		1.78	1.70		2.10	1.97	3.77* (ddd, H5'a, J=13.8, 7.0, 5.0); 3.75* (ddd, H5'b, J=13.8, 6.5, 4.8); 1.97-1.85 (m, H3', H4')
18by	-$OCH_2CH_2CH_2$-		1.72	2.51	1.83	5.53	5.32	2.0 - 1.65		2.0 - 1.65		1.97		1.90	2.11	3.81 (dd, H5', J=6.8, 6.3); 1.98-1.86 (m, H4'); 1.78-1.70 (m, H3')

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
10by	OH	H	6.0	6.8	-	-	6.8	2.1	5.3	-	-	6.5	-	6.5	8.3	8.8	4.2	
11bx	CH_3	OH	6.3	7.5	-	-	6.5	2.1	5.3	5.6	0.0	6.6	11.9					
11by	OH	CH_3	6.6	6.7	-	-	6.7	2.3	5.3	4.5	2	6.9	12.2					b,e=+
12bx	iPr	OH	6.4	6.6	-	-	6.6	2.2	5.3	-	-	6.2	11.9					b,e=+; i_b,k_b=1.6
13by	OCH_3	H	6.3	6.9	-	-	6.6	2.3	5.3	4.4	1.8	6.4	10.7	6.4	8.4	8.7	4.1	
14bx	CH_3	OCH_3	6.3	-	-	-	6.3	2.2	5.3	6.1	0.0	6.1	12.1					i_b,k_b=1.3
14by	OCH_3	CH_3	6.9	6.5	-	-	6.5	2.3	5.3	3.9	0.0	6.1	11.8					b,e=+; i_b,CH_3=+, k_b,CH_3=+
15b	CH_3[c]		6.2	6.8	-	-	6.7	2.2	5.3	-	-	-	-	-	-	-	-	
16b	CH_3	CH_3	6.5	6.5	-	-	6.5	2.2	5.3	4.8	0.0	6.8	12.0					i_a,CH_3=+; k_a,CH_3=+
17b	iPr[c]		6.4	6.8	-	-	6.8	2.2	5.3	-	-	-	-	-	-	10.1	6.9	b,e=+; c,e=+
18bx	-$CH_2CH_2CH_2O$-		6.3	6.9	-	-	6.7	2.2	5.3	5.5	0.0	7.1	11.5					b,e=+; i_a,k_a=1.2
18by	-$OCH_2CH_2CH_2$-		6.8	6.4	-	-	6.3	2.2	5.3	-	-	-	10.7					b,e=+

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

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
10cx	H	OH	1.39	2.42	5.73	5.50	2.26	2.37	1.54	1.86	1.83	2.07	4.28	1.82	2.69	
10cy	OH	H	0.85	2.40	5.67	5.47	2.37	2.43	1.64	1.67	2.10*	1.54*	4.18	2.19[+]	2.08[+]	
11cx	CH_3	OH	1.48	2.39	5.74	5.50	2.24	2.33	1.56	1.91	1.86	1.86		1.85*	2.46*	1.29 (s, CH_3)
13cx	H	OCH_3	1.30	2.41	5.72	5.48	2.29	2.36	1.47	1.80	2.02	- 1.88	3.69	2.02-1.88	2.50	3.28 (s, OCH_3)
13cy	OCH_3	H	0.84	2.39	5.67	5.48	2.37	2.44	1.58	1.65	2.12	1.52	3.71	2.25	2.03	3.36 (s, OCH_3)
18cx	-$CH_2CH_2CH_2O$-		1.48	2.39	5.72	5.49	2.28	2.35	1.50	1.91	1.80*	1.93*		1.94	2.27	3.90-3.78 (m,H5'); 1.91-1.75 (m, H4'); 1.91-1.63 (m, H3')
18cy	-$OCH_2CH_2CH_2$-		0.97	2.42	5.69	5.50	2.55	2.40	1.54	1.72	1.91	- 1.78		1.92*	2.65*	3.78 (m, H5'); 2.12 (m, H3'a); 2.01-1.90 (m, H4'); 1.81 (m, H3'b)

adduct	R_1	R_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
10cx	H	OH	6.6	2.8	6.5	2.3	5.8	2.6	3.0	0.0	4.2	4.4	2.0	6.1	2.0	4.8	c,f=2.5; c,e=0.8; f,h_b=2.7; h_a,i_b=1.4
10cy	OH	H	6.5	3.0	6.4	2.3	5.8	2.5	-	0.0	3.0	3.2	6.6	9.9	6.9	8.8	a,d=+; c,e=0.8; h_a,i_b=1.2
11cx	CH_3	OH	6.6	2.7	6.6	2.4	5.8	2.6	3.6	2.6	3.4	3.4					c,f=2.6; k_b,CH_3=+; h_a,k_a=+
13cx	*H*	*OCH*$_3$	6.5	2.8	6.5	2.4	5.8	2.6	3.0	0.0	3.0	3.0	1.9*	5.2	3.6*	5.0	c,h_b=2.4; c,e=0.8; f,g=3.0
13cy	OCH_3	H	6.6	3.0	6.4	2.4	5.8	2.6	3.3	0.0	3.0	3.2	6.6	9.7	6.9	8.7	c,e=+
18cx	-$CH_2CH_2CH_2O$-		6.5	2.5	6.5	2.4	5.8	2.5	-	-	3.7*	-*					c,e=0.8; c,f=2.4; f,i_b=0.7; i_a,k_a=1.2
18cy	-$OCH_2CH_2CH_2$-		6.5	3.0	6.5	2.2	5.8	2.5	3.5	0.0	-	-					c,e=0.9; f,h_b=2.5; f,i_b=0.6

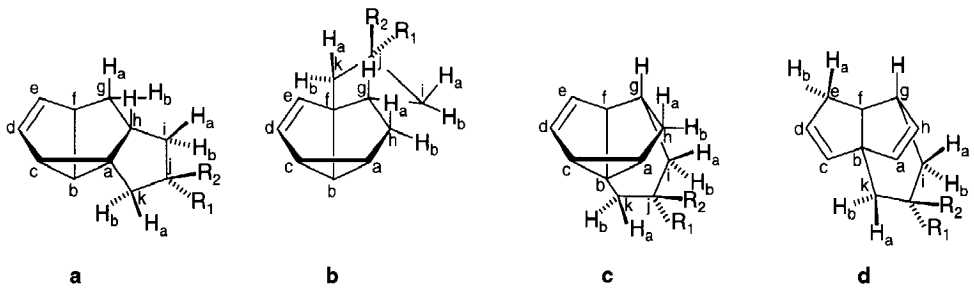
Table 1d 300 MHz ^{1}H chemical shifts (ppm) and coupling constants (Hz) ($CDCl_3$, TMS) of adducts of type **d**.[b,c]

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
15dx	H	CH_3	5.28	5.78	- 5.73	2.03-1.92*	2.27*	2.03-1.92	2.57	5.78-5.73	1.35	1.81	1.98	1.56	1.75	1.09 (d, CH_3, J=7.6)
15dy	CH_3	H	5.24	5.77	5.72	1.97*	2.23*	1.72	2.62	5.66	1.59	1.00	1.76	1.81	0.93	0.91 (d, CH_3, J=6.6)
17dx	H	iPr	5.29	5.78	5.76	1.95*	2.24*	2.32	2.57	5.80	1.79 -	1.40	1.6-0.8	1.79 -	1.40	1.52 (m, $C\underline{H}(CH_3)_2$); 0.82 (d, both CH_3, J=6.3)
17dy	iPr	H	5.23	5.78	5.73	1.98*	2.23*	1.69	2.64	5.66	1.60	1.08	1.40	1.81	1.00	1.42 (m, $C\underline{H}(CH_3)_2$); 0.85 (d, both CH_3, J=6.3)

adduct	R_1	R_2	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
15dx	H	CH_3	5.5	-	-	0.0*	-	1.7*	-	11.0	3.1	2.3	3.7	2.2	8.8	2.0	8.8	a,f=0.5; j,CH_3=7.6
15dy	CH_3	H	5.5	5.7	2.7	1.1	1.5	2.7	9.1	7.9	2.8	3.5	2.5	6.3	10.5	6.2	10.5	a,c=0.9; h,i_a=1.1
17dx	H	iPr	5.7	5.7	2.6	1.0	1.5	2.5	8.4	7.7	2.7	-	-	-	-	-	-	
17dy	iPr	H	5.6	5.7	2.7	1.2	1.6	2.7	8.8	8.0	2.8	3.6	2.5	5.8	10.2	5.7	10.5	f,h=0.8; f,g=+

[a] The signs * and + indicate that these values may be interchanged; Ha and Hb indicate the endo and exo hydrogen atom, respectively.

[b] Lettering of the adducts:



a **b** **c** **d**

[c] Stereochemistry unknown.

β-position (and hydroxyl group at γ-carbon atom) also induced cyclization (factor of 240 to compound without t-butyl) and the rate of the hydroxyl/t-butyl compound was accelerated 60 times with respect to that of the alkane analogue, implying a combined effect of the OH and t-butyl group[6b]. According to Sternbach and coworkers[7] this is due to the "reactive rotamer effect". These authors also found cyclization to occur with mono-β-substituted methyl-, phenyl- and t-Bu-sulfonyl derivatives.

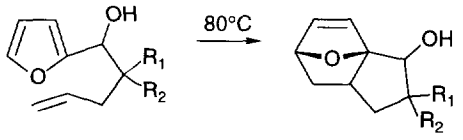


Figure 4 Diels-Alder reaction of α-(1,1-R_1,R_2-3-butenyl)-2-furanmethanol.

Recently, Parrill and Dolata[8] published evidence against the reactive rotamer explanation being the major contributor to the gem-dialkyl effect: a plot of reaction rate versus reactive rotamer population was not linear at all. Calculations showed, however, that the overall activation enthalpy was reduced by disubstitution. Evidently, disubstitution favours a conformation, which resembles the conformation for 1,3 addition. No rate enhancement is found in our case (see below). One reason might be that favouring the conformation necessary for addition also favours quenching.

The alkyl substituted compounds, entries **15** and **17** in Table 2, show that the larger group, isopropyl, induces only slightly less 2,6 addition than the smaller group, methyl. Moreover, the 2,6 : 1,3 ratio of the methyl derivative is not significantly different from that of the unsubstituted derivative **19**, which means that the methyl group either does not sterically hinder both modes of addition or hinders them to the same extent.

Table 2 2,6 versus 1,3 addition of 4,4-R_1,R_2-5-phenylpent-1-enes **10** - **18** and **P**.

compound	R_1	R_2	% 2,6	% 1,3	2,6 : 1,3
P	H	H	72[a]	28[a]	2.6 : 1
10	H	OH	44	33	1.3 : 1
11	CH_3	OH	6	81	1 : 13.5
12	$CH(CH_3)_2$	OH	0	83	0 : 1
13	H	OCH_3	52	30	1.7 : 1
14	CH_3	OCH_3	≤ 17	79	≤ 1 : 4.4
15	H	CH_3	71	20	3.6 : 1
16	CH_3	CH_3	0	69	0 : 1
17	H	$CH(CH_3)_2$	53	< 26	> 2.0 : 1
18	$-OCH_2CH_2CH_2-$		10	63	1 : 6.3

[a] Normalized to 2,6 + 1,3 = 100% [2]

The OH derivative **10** has greater preference for 1,3 addition than the methyl derivative **15** and the unsubstituted derivative **19**. This implies the presence of an electronic effect, which either stimulates 1,3 addition or disfavours 2,6 addition or both. When a second β-substituent is introduced in the OH derivatives, as in **11** and

12, there is only a negligible amount of 2,6 addition like in the dimethyl derivative **16**, which means that the electronic effect of OH is not manifested and probably overruled by steric factors. To investigate if the possible electronic effect of OH is a repulsion between the oxygen lone pairs and the π-electrons of benzene or attraction between the proton and the π-electrons, two methoxy derivatives and one tetrahydrofuran derivative were investigated. The methoxy derivatives, **13** and **14**, gave similar 2,6 : 1,3 ratios as their hydroxy analogues, **10** and **11**, respectively. The 2,6 : 1,3 ratio of **18** does not differ significantly from the ratio of the methoxymethyl derivative **14**. Only repulsion seems to be important for the 2,6 : 1,3 ratio.

To investigate whether the observed variations in the 2,6 : 1,3 ratios are due to promotion of 1,3 addition with respect to 2,6 addition by the various substituents or to obstruction of 2,6 addition in favour of 1,3 addition, relative reaction rates of compounds **10** - **15** were determined in cyclohexane. All irradiations were performed in a Merry-go-round apparatus and compound **4**[1] was used as external standard in order to be able to correct for variations in light intensity. Compounds **10**, **11**, **14** and **15** were also irradiated in methanol. The rates of disappearance of the starting material and the total formation of products presented in Table 3 are rather constant whatever substituent is present. The data also show that when the rate of 2,6 addition decreases the rate of 1,3 addition increases, and vice versa. This implies that the step leading to addition has already been made before the mode of addition is chosen. But the question if this choice is determined by retarding 2,6

Table 3 Rates in nmol/ml/min (relative to **4**) of disappearance of starting material and formation of products for some 4-R_1-4-R_2-5-phenylpent-1-enes in cyclohexane and methanol.[a]

				1,3 adducts				2,6 adducts		
	R_1	R_2	r_D[b]	$r_{l,n}$[c]	$r_{l,x}$[c]	$r_{a,n}$[c]	$r_{a,x}$[c]	r_{endo}	r_{exo}	r_{tot}
4[f]	ring	OH	35.1	15.6	-	9.2	-	0.6	0.4	25.8
10[f]	H	OH	31.8	1.5	3.4	1.5[h]	3.7	4.8	5.8	20.7
11[f]	CH_3	OH	30.5	7.2	1.9	5.5	1.7	1.0		17.3
12[f]	iPr	OH	35.1	10.5	-	8.5	-	-	-	19.0
13[f]	H	OCH_3	36.5	-	4.0	-	5.2	6.5	8.1	23.8
14[f]	CH_3	OCH_3	28.7	2.4	7.8	3.7	7.4	1.6[d]		22.9
15[f]	H	CH_3	33.0	6.1[e]				8.5	7.9	22.5
10[g]	H	OH	27.1	-	3.0	-	2.6	3.6	4.5	13.7
11[g]	CH_3	OH	26.6	1.6	5.1	2.0	4.5	≈0.3		13.5
14[g]	CH_3	OCH_3	26.6	2.2	7.9	2.9	6.8	1.1[d]		20.9
15[g]	H	CH_3	31.6	5.8[e]				9.0	7.5	22.3

[a] estimated errors in measured values ≤ 15%
[b] r_D = rate of disappearance of starting material
[c] r = rate of formation, l = linear, a = angular, n = endo-R_2 and x = exo-R_2
[d] total rate of 2,6 addition, configuration unknown
[e] total rate of 1,3 addition, one linear and one angular adduct with unknown configuration
[f] irradiated in cyclohexane
[g] irradiated in methanol
[h] this compound was not isolated, but was assumed to be the second angular adduct, **10bx**, consistent with retention time on AGC and ratio of other 1,3 adducts (**10ay** : **10by** = 1:1.1)

addition or by accelerating the 1,3 addition still stands.

Irradiation in methanol seems to be a bit slower although the values for the methyl compound **15** and the methoxy compound **14** do not differ significantly from those in cyclohexane. The total rate of formation of products, however, for the hydroxy derivatives **10** and **11** is significantly less in methanol than in cyclohexane. Irradiation in methanol showed no significant solvent effect on the 2,6 : 1,3 ratio. The effect of the solvent on the ratio of endo/exo orientation of the substituents will be discussed below.

Exo/endo 2,6 addition

When 2,6 addition occurs, always both orientations of the substituent are found in comparable amounts, exo as well as endo, while with 1,3 addition the endo/exo ratio varies substantially, depending on the substituent. Obviously 2,6 addition has other steric requirements than 1,3 addition. In the literature the interconnecting chain in 2,6 addition is sometimes drawn in conformation **A**[4,9,10,11,12] and sometimes as **B**[2,10b] (Figure 5). But no attention has thus far been paid to the possible consequences of the existence of two conformations for the 2,6 photoaddition as proposed in our previous article[1]. The number of eclipsed interactions

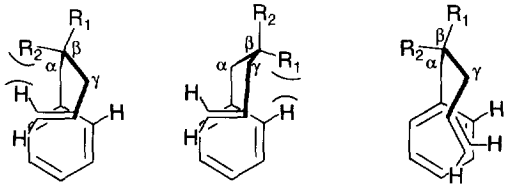


Figure 5 Possible conformations for 2,6 addition (with one substituent at the β-carbon atom) and 1,3 addition.

in conformations **A** and **B** is about the same. In **A** the conformation at carbon atoms α and β is more eclipsed than at carbons β and γ, while in **B** the situation is reversed. The percentages of exo- and endo-substituted 2,6 adducts from four mono-β-substituted 5-phenylpent-1-enes are given in Table 4. These four compounds give nearly equal amounts of exo- and endo-substituted 2,6 adducts, independent of the size of the substituent, which is due to the existence of two conformations. The conformation most frequently encountered in the literature, **A**, can not be responsible for this phenomenon, because a severe interference between the substituent and a terminal vinylic proton is present when the substituent is endo (structure **A2**), whereas the same conformation with the substituent exo has no steric interference of the substituent (structure **A1**). The only way in which addition with the substituent endo can take place is when the β-carbon is flapped away as in conformation **B2**, like the flap of the envelope conformation of a cyclopentane ring (exo β-C conformer).

In conformation **B**, however, there is steric interference between an exo-β-substituent and an ortho phenyl proton (structure **B1**). When two substituents are present there is steric hindrance in both conformations, resulting in predominantly or exclusively 1,3 addition.

Table 4 Exo versus endo 2,6 addition of 4-R-5-phenylpent-1-enes.

compound	R	exo	endo	exo : endo
10	OH	23	21	1.1 : 1
13	OCH_3	30	22	1.4 : 1
15	CH_3	33	38	1 : 1.2
17	$CH(CH_3)_2$	24	29	1 : 1.2

To support the above hypothesis - exo-substituted adduct formed via **A1** and endo-substituted adduct via **B2** - we have performed some preliminary calculations on the geometry of the connecting chain required for 2,6 addition in the ground state. Although the actual reaction takes place in the electronically excited state, we feel justified in using ground state calculations in this first attempt at trying to understand which geometrical factors are of importance. First, the properties of the saturated connecting chain will not or only very slightly be influenced by electronic excitation of the phenyl ring. Second, at this early stage of the reaction there is interaction between the π-electrons of the addends, but the formation of chemical bonds has not yet started and the benzene ring, although more flexible than in the ground state, is not yet severely distorted.

Using the molecular mechanics method, MM2[13] (not specially parametrized for aromatic systems) incorporated in the Model-program, a starting structure with rotational minima for each of the side chain bonds was calculated, selecting those minima which yield the 2,6 cycloaddition conformation, corresponding to **A**. Subsequently, the dihedral angle C2-Cε-Cδ-C6 was fixed at 0°, the structure was optimized and used as starting structure for further calculations, MM and semiempirical. For the semiempirical molecular orbital method PM3 parameters[14] were chosen, because they reproduce experimental rotational barriers in branched alkanes better than AM1 and MNDO, although the barriers are often still underestimated[15]. For the semiempirical calculations the phenyl ring and the alkene were defined with respect to each other with the help of two dummy-atoms at a distance of 3.0 Å (just beyond interaction between alkene and excited benzene[16], one in the middle of the double bond and the other halfway between C2 and C6 of the phenyl ring; only movement of the double bond along the line C1-C4 was possible. Optimization of this structure of 5-phenylpent-1-ene gave a starting structure for the substituted compounds. The substituted structures were reoptimized under the same conditions for each staggered substituent rotamer and the mean was calculated using the Boltzmann distribution equation[17] (all conformations are thermally accessible). Also calculations with a free double bond were performed in which the alkene dummy-atom was completely set free and the alkene can move anyway it likes. The dihedral angles in the benzene ring were kept at 0°, because otherwise the benzene ring becomes distorted. Otherwise, the method of calculation was the same as for the fixed double bond. The conformer with exo Cβ was constructed from the calculated **A** with the conformation of the connecting chain changed: Cβ-Cα-C1-C6 at -55° and Cγ-Cβ-Cα-C1 at -60° (estimated from Darling molecular models), which is justified by the values found. Optimization of this structure under the same constraints as for **A** resulted in the calculated conformer **B** for 5-phenylpent-1-ene. From **B** the same strategy as for **A** was followed for fixed and free double bond.

For the 2,6 addition from the **A** conformation the MM2 and PM3 results, for a fixed double bond and for a free double bond are presented in Table 5. The differences between the heats of formation for the endo (R_2) and exo (R_1) substituted conformation for the fixed alkene show a large preference for the substituent in the exo position in both calculational methods, MM2 and PM3. In the structures calculated with PM3 with the alkene fixed the β-carbon appeared to bend away from the phenyl ring; the β-carbon cannot move away

completely, because of the rotational barrier preventing it to reach conformation **B**. In the structure with a free double bond the addition with the substituent endo still is the least favourable just as in the fixed situation. From the calculations it can be seen that in the optimization the connecting chain retains the conformation **A** (or **B**) that was originally imposed, but in both conformations the alkene turns away from the phenyl ring to a distance of 3.5 - 4.0 Å. When the alkene is free to move, the position and the nature of the substituent have a larger influence on the optimized geometry of the molecule than when the alkene is fixed. Also in the situation with a free double bond the difference between the energies of the structures with endo and exo substituent is larger than when the double bond is fixed.

Table 5 MM2 heats of formation with alkene fixed and PM3 heats of formation with alkene fixed and alkene free for 2,6 addition in the **A** conformation (kcal/mol).

compound			MM2		PM3(alkene fixed)		PM3(alkene free)	
	R_1 (exo)	R_2 (endo)	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]
19	H	H	21.81		31.75		28.03	
15	CH_3	H	22.67		27.99		21.89	
	H	CH_3	24.17	1.50	29.74	1.75	27.76	5.87
13	OCH_3	H	28.19		-2.25		-5.64	
	H	OCH_3	30.17	1.98	-0.81	1.44	-0.94	4.70
10	OH	H	23.21		-7.86		-10.92	
	H	OH	24.65	1.44	-7.42	0.44	-9.91	1.01
17	$CH(CH_3)_2$	H	-		18.13		15.04	
	H	$CH(CH_3)_2$	-	-	20.14	2.01	18.78	3.74

[a] $\Delta\Delta H_f = \Delta H_f$(endo) - ΔH_f(exo)

In Table 6 the heats of formation of the conformations with the β-carbon bent away from the alkene are listed. These show a clear preference for the structure with the substituent endo, as expected, because the exo substituent has steric hindrance with the ortho proton of the phenyl ring (see Figure 5). In these **B** conformations the double bond is forced away in the direction of C1. In the last column of Table 6 the fixed alkene conformations for comparison were chosen, because for the **A** conformation with free alkene only the dihedral angle C1-C2-C3-C4 was optimized, while for the **B** conformation with free alkene also the dihedral angles C5-C4-C3-C2 and C3-C4-C5-C6 of the benzene ring were optimized, allowing C1 to bend downwards. All four substituents show a similar difference in $\Delta\Delta H_f$ consistent with the experimental finding (Table 4) that the amounts of exo and endo substituted 2,6 adducts are independent of the size of the substituent. The value for 5-phenylpent-1-ene is about 1.7 kcal/mol higher than for the substituted compounds. In this molecule the conformation with the β-carbon atom folded away (as in conformation **B**) is higher in energy than the conformation with the β-carbon atom towards the alkene (as in conformation **A**). If this is also the case in cis-6-phenylhex-2-ene it is still understandable why this compound does not undergo 2,6 addition[18,19], which was ascribed to steric hindrance between the methyl group and a β-hydrogen atom[19]. Apparently, flapping away of

the β-carbon atom does not play a significant role for this compound, because otherwise some 2,6 addition would certainly occur. It seems that the **B** conformation becomes important only when a β-substituent is present.

Table 6 PM3 heats of formation for 2,6 addition in the **B** conformation with fixed and free alkene (kcal/mol).

compound			alkene fixed		alkene free		
	R_1 (exo)	R_2 (endo)	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]	$\Delta\Delta H_f$[b]
19	H	H	32.45		26.33		+0.70
15	CH_3	H	28.10		24.03		
	H	CH_3	27.02	-1.08	21.04	-2.99	-0.97
13	OCH_3	H	-1.06		-2.98		
	H	OCH_3	-3.46	-2.40	-9.10	-6.12	-1.21
10	OH	H	-7.95		-13.71		
	H	OH	-9.02	-1.07	-15.25	-1.54	-1.16
17	$CH(CH_3)_2$	H	18.93		13.33		
	H	$CH(CH_3)_2$	17.11	-1.82	10.69	-2.64	-1.02

[a] $\Delta\Delta H_f = \Delta H_f(\text{endo}) - \Delta H_f(\text{exo})$

[b] $\Delta\Delta H_f$ = difference in heat of formation of the endo substituted conformation with the β-carbon folded away (= **B2**; this Table) and the exo substituted conformation with the β-carbon atom towards the alkene (= **A1**; from Table 5) for fixed double bond

Exo/endo 1,3 addition

In the 1,3 photoaddition mode the endo/exo ratios are influenced significantly by the substituent(s) at the β-position, as can be seen from the first five entries in Table 7. On the whole it can be said that the largest

Table 7 Ratios of endo/exo 1,3 photoaddition of 4,4-R_1,R_2-5-phenylpent-1-enes in cyclohexane and methanol, derived from the relative rates of formation in Table 3.

compound	R_1	R_2	exo : endo
10[a]	H	OH	2.4 : 1
11[a]	CH_3	OH	1 : 3.5
12[a]	iPr	OH	0 : 1
13[a]	H	OCH_3	1 : 0
14[a]	CH_3	OCH_3	2.5 : 1
10[b]	H	OH	1 : 0
11[b]	CH_3	OH	2.7 : 1
14[b]	CH_3	OCH_3	2.9 : 1

[a] in cyclohexane

[b] in methanol

substituent prefers the exo position in the adduct, which is the least sterically hindered. The methoxymethyl derivative **14**, however, has the methoxy group, which is sterically less demanding than the methyl group (as judged on the basis of axial-equatorial free-energy differences in cyclohexane[20]), predominantly in the exo configuration. Likewise, the tetrahydrofuran derivative **18** (Figure 1) affords predominantly adducts with the oxygen atom exo (endo : exo = 1 : 2.7). The exo position of oxygen in both compounds might be preferred because the endo approach suffers from repulsive interaction between the oxygen lone pairs and the π-electrons of the alkene or phenyl ring. Houk and co-workers[21] have recently theoretically investigated the repulsion between lone electron-pairs and π-electrons in the Diels-Alder reaction. By means of ab initio calculations on the transition state they found that a structure with exo lone pairs is ≥ 4 kcal/mol more stable than that with endo lone pairs, as a consequence of the repulsion. A similar effect is probably important in the reactions of compounds **14** and **18**. In agreement with these considerations, the monomethoxy derivative **13** affords only exo methoxy 1,3 adducts. The monohydroxy derivative **10**, however, yields also 1,3 adducts with the hydroxyl group in the endo configuration (endo : exo = 1 : 2.4). This is neither expected on the basis of the steric demands of the hydroxyl group as compared to those of the methoxy group (again as judged from conformational free energy differences: 0.52 kcal/mol for OH and 0.60 kcal/mol for OCH_3[20]) nor on the basis of the repulsive effects mentioned above. A possible explanation is the presence of a hydrogen bond between the hydroxyl group and the π-electrons of the phenyl ring, which would favour the conformation with the hydroxyl group endo.

Intramolecular hydrogen bonding between a hydroxyl group and a π-electron system is well-known from the literature. In 1959 a study was published by von R. Schleyer et al.[22] on the infrared spectra of β-arylethanols. These compounds display two absorption bands in the 3650 - 3580 cm^{-1} region. Bakke[23] has also studied β-arylethanol derivatives and found that the gauche rotamers dominate the conformational equilibrium (≥ 85 %) as deduced from the $^3J_{CH\text{-}OH}$ NMR coupling constant. The integrated areas of the two IR bands were, however, about 1 : 1. It was concluded that both O-H stretch bands in the IR spectrum had to be assigned to gauche rotamers, one with a hydrogen bond between the hydroxyl group and the phenyl ring and the other with a free hydroxyl group - and not to a gauche and anti rotamer as is found frequently in saturated alcohols. Calculations on the different conformations of 2-phenylethanol using molecular mechanics and semiempirical as well as ab initio MO methods performed by Bakke and Chadwick[24] proved this conclusion: the hydrogen bonded, major conformer (ca. 45%) was stabilized to the extent of 1.2 kcal/mol over the other ones. In the bark beetle pheromones ipsenol and ipsdienol, Bakke et al.[25a] have found structures in which the hydroxyl group - again two CH_2 groups away from the π-system - is hydrogen-bonded to a butadiene fragment. They also noticed that the conformation in methanol is different from that in CCl_4 or $CFCl_3$ and they ascribed this to replacement of an intramolecular hydrogen bond by intermolecular hydrogen bonds with the solvent methanol. A similar frequency difference was found for 3-buten-1-ol[25b].

Following Bakke[23,24] we have measured the infrared spectra of the alcohols **10** - **12** in an inert solvent (CCl_4) at concentrations of 5 mM. The results, together with some data from the literature are presented in Table 8. Our compounds also have their hydroxyl groups at the β-position with respect to the phenyl ring and alkene, and indeed two O-H stretch frequencies are observed with frequency differences comparable to those found by Bakke. This implies that also in our compounds a hydrogen bond between OH and phenyl or/and alkene might be present, if we assume that they also have a gauche conformation around the C-O bond like in 1-phenyl-2-propanol. From the calculations described below the staggered conformations with the OH endo and with the alcohol proton pointing in between the alkene and benzene ring is for the 1,3 addition with free alkene the most stable of the exo and endo conformations for **11** and **12**, while for **10** it is 0.18 kcal/mol above the most stable one. For the monohydroxy derivative in all calculation methods this conformation is the second stable one lying

0.18-1.13 kcal/mol above the most stable one. But this can still be the effect of repulsion of the lone pairs. It should be realized that these results all pertain to the molecules in their ground electronic state and that it is unknown whether hydrogen bonds between a hydroxyl group and a phenyl ring become stronger or weaker upon excitation.

Table 8 OH stretch vibrations of alcohols **10**, **11** and **12** (in CCl_4) and some literature data for unsaturated alcohols in $CCl_4/CFCl_3$ at concentrations < 10^{-2} M.

compound	ν_1 (cm^{-1})	ν_2 (cm^{-1})	$\Delta\nu$ (cm^{-1})
10[a]	3615	3597	18
11[a]	3610	3588	22
12[a]	3615	3586	29
2-phenylethanol[a]	3632	3604	28
„ [b]	3630	3601	29
2-phenylpropanol[b]	3637	3601	36
1-phenyl-2-propanol[b]	3620	3598	22
3-buten-1-ol[c]	3635	3596	39
ipsenol[d,e]	3627	3592	35
ipsdienol[d]	3617	3583	34

[a] present study
[b] from reference 23
[c] from reference 25b
[d] from reference 25a
[e] a third band was present at 3606 cm^{-1} assigned to the anti conformer around the C-O bond

Semiempirical PM3 calculations were executed in the same manner as for 2,6 addition, with the double bond fixed as well as free in 1,3 position above the phenyl ring. The results are presented in Table 9. For the monoalkyl derivatives **15** and **17** the calculations predict a preference for addition with the alkyl group in the exo conformation. Unfortunately, the configurations of the substituents in the 1,3 adducts from these compounds could not be determined, but each type of 1,3 adduct was formed in only one configuration which is likely to be exo. For compounds **10** - **14** the results of the calculations are in agreement with the experimental observations.

We have not performed calculations on the 1,3 addition in the conformation with the β-carbon atom pointed towards the alkene, because in that conformation a β-hydrogen atom has steric interaction with an ortho phenyl proton, while the other conformation does not suffer from any appreciable steric hindrance. Moreover, a very strong preference for this conformation was also found for 1,3 addition of the cycloalkane derivatives[1].

Concerning the Thorpe-Ingold effect[26] - a smaller bond angle caused by disubstitution -it is worth mentioning that we compared the structures **A1** and **B2** for 2,6 addition with the 1,3 addition conformations with substituent exo. For the 2,6 conformations - all monosubstituted - a bond angle of 115-116° was calculated for C3-C4-C5. Smaller angles were found in the 1,3 conformations for the disubstituted (112°) as well as for the monosubstituted compounds (113°). This smaller bond angle may favour the 1,3 mode of addition. The bond angle difference between the methylmethoxy derivative **14** and the THF derivative **18** is nil in the optimized structures calculated and indeed, experimentally no difference in ratios was found (Table 2).

Table 9 PM3 heats of formation (kcal/mol) of conformations with free and fixed alkene leading to 1,3 addition.

compound			alkene fixed		alkene free	
	R_1 (exo)	R_2 (endo)	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]
15	CH_3	H	25.42		21.18	
	H	CH_3	27.28	1.86	23.27	2.09
17	iPr	H	-		11.11	
	H	iPr	-	-	15.05	3.94
10	OH	H	-10.70		-13.97	
	H	OH	-10.28	0.42	-13.82	0.15
13	OCH_3	H	-4.65		-8.45	
	H	OCH_3	-2.23	2.42	-5.44	3.01
11	OH	CH_3	-14.03		-18.03	
	CH_3	OH	-15.11	-1.08	-18.90	-0.87
14	OCH_3	CH_3	-7.25		-11.16	
	CH_3	OCH_3	-6.20	1.01	-9.70	1.46
12	iPr	OH	-		-27.27	
	OH	iPr	-	-	-26.17	1.10
18	$-OCH_2CH_2CH_2-$		-		-11.75	
	$-CH_2CH_2CH_2O-$		-	-	-8.81	2.94

[a] $\Delta\Delta H_f = \Delta H_f(\text{endo}) - \Delta H_f(\text{exo})$

Solvent effects

When the endo/exo ratios of the 1,3 photoadducts from compounds **10** and **11** in cyclohexane are compared with those in methanol (Table 7), a solvent effect is apparent. The effect is strongest for the hydroxymethyl derivative **11**: in cyclohexane the hydroxyl group in the adduct is predominantly endo (3.5 : 1), whereas in methanol it is predominantly exo (1 : 2.7). This effect can be explained by solvation. In cyclohexane, the methyl group is the largest substituent and the smaller hydroxyl group prefers the endo position. In methanol the hydroxyl group is solvated and becomes effectively larger than the methyl group, resulting in a preference for addition with OH exo. In compound **10** the effect is smaller. The ratio endo-OH/exo-OH is 1 : 2.4 in cyclohexane and becomes 0 : 1 in methanol. In this case in cyclohexane solution the hydroxyl group is already the larger substituent. Hydrogen bonding between the hydroxyl group and the phenyl ring might be responsible for the occurrence of some endo addition in this solvent. If this hydrogen bonding exists, it will certainly be replaced by hydrogen bonding between the hydroxyl group and methanol if the latter is used as solvent. This will effectively enlarge the hydroxyl group and direct the addition fully towards the exo mode. Irradiation of compound **11** in tetrahydrofuran caused a similar, though somewhat smaller, effect as in methanol: the endo-OH/exo-OH ratio is 1 : 2 and also in this case hydrogen bonding between the hydroxyl group and the solvent might be responsible. The methoxymethyl derivative **14** was also irradiated in both cyclohexane and methanol. In this case the solvent effect is negligible (see Table 7). Also the hydroxyl group of compound **11**

was deprotonated in tetrahydrofuran by adding 1 eq. sodium hydride or methyllithium. Meta photocycloaddition still took place, accompanied by some dehydration (2% with NaH and 10% with CH_3Li). The degree of deprotonation was estimated by measuring the intensity of the OH stretch vibration at ca. 3500 cm^{-1} (free and bonded OH) in the IR spectrum. With NaH compound **11** was deprotonated for ca. 30%, with CH_3Li for more than 90%. The ratio endo-OH/exo-OH was found to be 1 : 2, the same as in the absence of NaH or MeLi. The deprotonated molecule can no longer form hydrogen bonds with the solvent, but its preference for addition with oxygen in the exo conformation might be related to repulsion between the negatively charged oxygen atom and the phenyl ring in the endo approach.

Concluding remarks

From the above results it can be concluded that the β-monosubstituted 5-phenylpent-1-enes always prefer 2,6 addition because of the stabilizing effect of the alkyl chain, independent of the size of the substituent. For 2,6 addition two basic conformations are possible, dependent on the position of the substituent: an endo-substituent will add with exo-β-C and an exo-substituent with endo-β-C, thus minimizing the steric interactions. With the β-disubstituted compounds 1,3 addition is always preferred, predominantly with the sterically more demanding group exo. For the methylmethoxy and THF derivative the oxygen is found at the exo position, which is ascribed to repulsion of the oxygen lone pairs with the π-systems in the endo position. The monohydroxy derivative, on the other hand, gives also some endo-hydroxyl adducts, which might be caused by hydrogen bond formation between the OH group and the phenyl ring. IR spectra of the hydroxyl derivatives indeed showed a ground state conformation to be present with a hydrogen bond between the hydroxyl group and the phenyl ring, which might still exist in the excited state. This hydrogen bond might also play a role in the addition of compounds **4** and **8** described in our previous article[1], which yield exclusively the adduct with the OH pointing towards the phenyl ring and not the one with the OH group pointing outwards. In compound **9** a similar effect might be present.

An inversion of the exo/endo hydroxyl ratio for 1,3 addition was observed when the hydroxymethyl derivative, **11**, was irradiated in cyclohexane and in methanol: the OH group changes from mainly endo in the apolar solvent to chiefly exo in the polar solvent, because solvation of the OH group reverses the relative size of the substituents.

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. Analytical gas chromatography was performed on a Packard 433 GC (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 Varian EM 360L spectrometer at 60 MHz, a Jeol FX-200 at 200 MHz or a Bruker WM300 spectrometer at 300 MHz 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 Jeol FX-200 at 50 MHz or a Bruker WM300 spectrometer at 75.5 MHz. The IR spectra of synthetical intermediates 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. NaH was obtained from Aldrich Chemicals N.V., Belgium as a 60% dispersion in oil and rinsed thoroughly with THF before use. CH_3Li was obtained from Aldrich Chemicals as a 1.6 M solution in diethyl ether.

The photoproducts of compounds **10** - **13** and **18** 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 (for the eluent see Table 11).

^{1}H NMR spectrometry of the photoadducts was performed on a Bruker WM300 operating at 300 MHz. ^{13}C NMR was performed on a JEOL FX200 or a Bruker WM300 operating at 50.1 MHz or 75.5 MHz, respectively. In some cases insufficient material (< 8 mg) was isolated to measure ^{13}C spectra. All spectra were recorded in $CDCl_3$ with TMS as internal standard. $Eu(FOD)_3$ was obtained from Merck. Trimethylsilyl derivatives were synthesized with 1-(trimethylsilyl)imidazole (TMSI, Aldrich) as described by Gleispach[27]. A mixture of 15 mg of the adduct and 0.6 ml TMSI was left at room temperature for 24 hrs. The excess of silylating agent was removed by a dry nitrogen stream and the residue was dissolved in hexane and further purified over silicagel using ether/hexane (1:1) as eluent. The EI (or $CI(NH_3)$) mass spectra were recorded on a Finnigan MAT 900 mass spectrometer.

Irradiations to determine the relative reaction rates at low conversion were performed in cyclohexane (Uvasol, Merck) or methanol (Uvasol, Janssen) in quartz vessels in a Merry-go-round apparatus with one Hanau TNN 15/32 Hg lamp at 19 - 23°C. The product ratios of compound **10** - **15** were determined relative to compound **4** in triplicate. The rate of disappearance of the starting material and formation of the products was first determined for compound **4** (6 measurements). During the first hour of the irradiation (less than 15% conversion) samples were taken and injected on GC. Solutions irradiated (under argon atmosphere) contained 15 mM substrate (8 ml) and internal standard (4 mM). As internal standards were used ethyl caprylate (Janssen) for compounds **12** - **14** and ethyl caprate (Janssen) for compounds **10**, **11** and **15**. The samples of compounds **12**, **14** and **15** were injected on an OV17 column and the samples of the other compounds were injected on an OV101 column as described above.

Infrared spectra were measured on a PE 580 IR spectrometer using CCl_4 (Aldrich) as solvent. The solutions were dried on molsieves (3 Å) before measurement. Concentrations of 5 mM were used in a 1 cm cuvette.

MM optimization was carried out using the program MODEL (version KS2.92), which includes an MM2-derived optimization mode. For the semiempirical calculations the PM3-parameters were used as implemented in the VAMP-program version 4.3 (based on AMPAC and MOPAC). Both programs are part of the facilities supplied by the CAOS/CAMM Center from the Catholic University Nijmegen.

Synthesis of the starting materials

5-Phenylpent-1-en-4-ol (10)

Phenylacetaldehyde (I): 3.0 g (18 mmol) 1,1-dimethoxy-2-phenylethane was deprotected with 0.4 g (1.8 mmol) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 126 ml acetonitrile/water (9 : 1) following Tanemura et al.[28]. After stirring overnight the solvent was evaporated and the red oily residue was purified by flash chromatography using ether/petroleum ether (1 : 1). Yield: 1.95 g 95% pure I (16 mmol; 90%). ^{1}H NMR (200 MHz): δ 9.73 (t, 1H, H1, J=2.5); 7.4-7.1 (m, 5H, aromatic); 3.67 (d, 2H, H2, J=2.5).

5-Phenylpent-1-en-4-ol (10): From 7.7 g (64 mmol) phenylacetaldehyde, 3.7 g (152 mmol) magnesium turnings and 14.0 g (116 mmol) allyl bromide in 300 ml THF 5-phenylpent-1-en-4-ol was synthesized following the Barbier-Grignard method[29]. 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 7.6 g (47 mmol, 73%) 5-phenylpent-1-en-4-ol (**10**) (95% pure on GC). UV (cyclohexane): λ_{max} 259, 253, 251 nm. ^{1}H NMR (200 MHz): δ 7.35-7.20 (m, 5H, aromatic); 5.87 (dddd, 1H, H2, J=17.5, 9.6, 7.7, 6.6); 5.16 (br d, 1H, H1Z, J≈17); 5.15 (br d, 1H, H1E, J≈10); 3.88 (dddd, 1H, H4, J=7.9, 7.6, 5.2, 4.8); 2.83 (dd, 1H, H5a, J=13.4, 5.2); 2.72 (dd, 1H, H5b, J=13.7, 7.9); 2.35 (dddt, 1H, H3b, J=13.9, 6.5, 4.8, 2x1.5); 2.21 (br dtt, 1H, H3a, J=14.1, 2x7.6, 2x1.0). ^{13}C NMR (50 MHz): δ 138.4 (quat. aromatic); 134.7 (C2); 129.4/128.4 (ortho and meta aromatic); 126.4 (para aromatic); 117.8 (C1); 71.7 (C4); 43.3 (C5); 41.1 (C3).

4-Methyl-5-phenylpent-1-en-4-ol (11)

Following the Barbier-Grignard method, 1.0 g (40 mmol) of magnesium, 3.6 g (30 mmol) allyl bromide and 2.9 g (22 mmol) benzyl methyl ketone in 60 ml THF were left stirring overnight. Work-up analogous to the method described in the synthesis of **10** yielded 3.7 g of a pale yellow oil containing 94% 4-methyl-5-phenylpent-1-en-4-ol (**11**). Further purification to 99% was achieved by HPLC (Zorbax-SIL column, eluent: 1% methanol/ 10% ether in petroleum ether). UV (cyclohexane): λ_{max} 265, 260, 254 nm. ^{1}H NMR (200 MHz): δ 7.38-7.24 (m, 5H, aromatic); 5.94 (ddt, 1H, H2, J=17.2, 10.2, 2x7.0); 5.18 (br dd, 1H, H1E, J=10.5, 2); 5.14 (br dd, 1H, H1Z, J=17.0, 2); 2.81 (d, 1H, H5a, J=13.0), 2.74 (d, 1H,

H5b, J=13.0); 2.26 (dd, 2H, H3a/H3b, J=7.0, 1.1); 1.25 (s, CH_3). ^{13}C NMR (50 MHz): δ 137.4 (quat. aromatic); 134.0 (C2); 130.5/128.1 (ortho and meta aromatic); 126.4 (para aromatic); 118.6 (C1); 72.0 (C4); 47.8 (C5); 46.2 (C3); 26.5 (CH_3).

4-Benzyl-5-methylhex-1-en-4-ol (12)

3-Methyl-1-phenyl-2-butanol (II): From 1.0 g (8.3 mmol) phenylacetaldehyde (I), 1.8 g (14.6 mmol) isopropyl bromide and 0.4 g (16.5 mmol) magnesium in THF 3-methyl-1-phenyl-2-butanol (XXIII) was synthesized analogous to the method described for **10**. Reaction overnight yielded 1.05 g yellow oil containing about 50% of the desired product, which was used as such in the next step. ^1H NMR (60 MHz): δ 7.3-7.1 (m, 5H, aromatic); 3.7 (q, H2, J=7); 2.98 (d, 2H, H1, J=7); 1.74 (m, 1H, H3); 0.98 (d, 6H, 2xCH_3, J=7).

3-Methyl-1-phenyl-2-butanone (III): The alcohol II was oxidized with the chromium trioxide-pyridine complex in methylene chloride following Ratcliffe et al.[30]. 1.05 g (6.7 mmol) alcohol yielded 0.8 g (4.9 mmol; 74%) ketone III as a yellow oil. ^1H NMR (200 MHz): δ 7.31-7.08 (m, 5H, aromatic); 3.73 (s, 2H, H1); 2.61 (m, 1H, H3); 1.08 (d, 6H, CH_3, J=7.2).

4-Benzyl-5-methylhex-1-en-4-ol (12): Following the Barbier-Grignard method 4-benzyl-5-methylhex-1-en-4-ol was synthesized from 0.8 g (4.9 mmol) of III, 0.25 g (10.3 mmol) magnesium and 1.1 g (9.1 mmol) allyl bromide in 25 ml THF. After stirring for two hours the reaction was carefully quenched with a saturated solution of ammonium chloride. Extraction of the water layer with ether, washing the combined ether layers with sodium bicarbonate and drying over $MgSO_4$ yielded 0.85 g of light yellow oil. Purification by silicagel chromatography using 10% ether in pentane yielded 450 mg 4-benzyl-5-methylhex-1-en-4-ol (**12**) in 99% purity (GC). UV (cyclohexane): λ_{max} 265, 260, 254 nm. ^1H NMR (200 MHz): δ 7.32-7.18 (m, 5H, aromatic); 5.85 (ddt, H2, J=17.0, 10.3, 2x7.2); 5.11 (br d, H1E, J=10); 5.06 (br d, H1Z, J=17); 2.85 (d, PhCHaHb, J=13.9); 2.66 (d, PhCHaHb, J=13.9); 2.28 (dd, H3a, J=14.1, 7.4); 2.06 (dd, H3b, J=14.4, 7.2); 1.81 (sept, H5, J=7.0), 1.35 (br s, OH); 1.01 (d, 3H, H6, J=6.7); 0.96 (d, 3H, CH_3, J=7.2). ^{13}C NMR (50 MHz): δ 137.5 (quat. aromatic); 134.0 (C2); 130.7/128.1 (ortho and meta aromatic); 126.3 (para aromatic); 118.3 (C1); 75.5 (C4); 41.4 (benzylic C); 40.7 (C3); 34.5 (C5); 17.0 (C6+CH_3).

4-Methoxy-5-phenylpent-1-ene (13)

2.0 g (12 mmol) Phenylacetaldehyde dimethylacetal, 3.1 g (27 mmol) allyltrimethylsilane and 5.5 g (24 mmol) zinc bromide in 50 ml dichloromethane were stirred overnight. The reaction was quenched with sodium bicarbonate and the organic layer was washed with 5% sodium hydroxide solution, 5% hydrogen chloride solution and brine. Drying over $MgSO_4$ and removal of the solvent yielded 1.84 g crude product (70% conversion). Column chromatography on silica (eluent: 6% ether in petroleum ether 40/60) resulted in 0.75 g (4.3 mmol; 36%) 4-methoxy-5-phenylpent-1-ene (**13**) (99% pure as measured on GC). UV (cyclohexane): λ_{max} 265, 260, 254 nm. ^1H NMR (200 MHz): δ 7.28-7.19 (m, 5H, aromatic); 5.85 (ddt, 1H, H2, J=17.7, 9.3, 2x7.0); 5.11-5.03 (double m, 2H, H1); 3.45 (br quin, 1H, H4, J=6.1); 3.31 (s, 3H, OCH_3); 2.83 (dd, 1H, H5a, J=13.8, 6.1); 2.72 (dd, 1H, H5b, J=13.8, 6.1); 2.24 (br t, 2H, H3, J=7). ^{13}C NMR (50 MHz): δ 138.9 (quat. aromatic); 134.7 (C2); 129.4/128.2/126.0 (aromatic); 117.1 (C1); 81.7 (C4); 57.0 (OCH_3); 39.8/37.5 (C3, C5).

4-Methoxy-4-methyl-5-phenylpent-1-ene (14)

Phenylacetone dimethylketal (IV): A suspension of 28 g K-10 Montmorillonite clay in a mixture of 16.5 ml trimethyl orthoformate and 20 ml methanol was stirred for 15 min. The clay was filtrated and added to a solution of 10.0 ml phenylacetone in 70 ml cyclohexane following Taylor and Chiang[31]. The suspension was stirred for 6 minutes, after which the clay was filtered off. The cyclohexane was washed with sodium carbonate and water, dried over $MgSO_4$ and the solvent was removed on the Rotavap. 6.4 g (48%) of ketal IV was obtained, still containing a few percent of starting material. ^1H NMR (60 MHz): δ 7.3 (m, 5H, aromatic); 3.3 (s, 6H, OCH_3); 2.95 (s, 2H, H1); 1.2 (s, 3H, CH_3).

4-Methoxy-4-methyl-5-phenylpent-1-ene (14): Analogously to the synthesis of compound **13** 2.1 g ketal IV and 2.8 g allyltrimethylsilane were added to a suspension of 4.2 g dry zinc bromide in 80 ml dry dichloromethane. The mixture was stirred for 5 hours, after which 100 ml water was added. Then the dichloromethane was washed several times with water and once with brine. Drying over $MgSO_4$ and removal of the solvent yielded 1.9 g crude product (86% desired product). Column chromatography on silicagel (eluent: 1.5% ether in petroleum ether 40/60) yielded 0.55 g (25%) 4-methoxy-4-methyl-5-phenylpent-1-ene (**14**) (98% pure on GC). UV (cyclohexane): λ_{max} 265, 259, 254 nm. ^1H NMR (300 MHz): δ 7.29-7.18 (m, 5H, aromatic); 5.89 (ddt, 1H, H2, J=17.0, 10.8, 2x7.2); 5.12 (ddt, H1E, J=10.8, 2.1, 2x1.4); 5.08 (ddt, H1Z, J=17.0, 2.1, 2x1.4); 3.30 (s, 3H, OCH_3); 2.77 (s, 2H, H5); 2.29 (ddt, 1H, H3a, J=14.4, 7.2, 2x1.4); 2.20 (ddt, 1H, H3b, J=14.5, 7.2, 2x1.4); 1.07 (s, 3H, CH_3). ^{13}C NMR (50 MHz): δ 138.1 (quat. aromatic); 134.3 (C2); 130.5/127.9/120.1 (aromatic); 117.6 (C1); 76.9 (C4); 49.2 (OCH_3); 43.7/42.0 (C5, C3); 22.4 (CH_3).

4-Methyl-5-phenylpent-1-ene (15)

2-Methyl-1-phenylpent-4-en-1-one (VIa): A solution of 6.6 g (49 mmol) propiophenone in THF was added dropwise to

a mixture of 40 ml THF and 3.5 g of a dispersion of sodium hydride in oil (60% w/w) in 40 ml THF. After one and a half hour of reflux 5.9 g (49 mmol) allyl bromide was added at once. After another two hours of reflux the reaction was quenched with 50 ml water. Ether extraction, washing of the combined organic layers with water and brine, drying over $MgSO_4$ and removal of the solvent resulted in 8.1 g of a yellow oil still containing 18% of starting material (used as such in the next step). ^{1}H NMR (200 MHz): δ 8.02-7.90 (m, 2H, ortho aromatic); 7.61-7.43 (m, 3H, meta and para aromatic); 5.79 (m, 1H, H4); 5.05 (br d, 1H, H5Z, J≈17.2); 5.01 (br d, 1H, H5E, J≈10.3); 3.54 (sext, 1H, H2, J=6.9); 2.57 (dtt, 1H, H3a, J=14.1, 2x6.5, 2x1); 2.19 (br dt, 1H, H3b, J=14.1, 2x7.0); 1.21 (d, 3H, CH_3, J=6.9).

4-Methyl-5-phenylpent-1-ene (15): 8.1 g (45 mmol) Ketone VIa, 5.6 g (112 mmol) hydrazine hydrate and 6.6 g (118 mmol) potassium hydroxide in 90 ml diethylene glycol were refluxed overnight[32]. The mixture was poured into 100 ml water, which was extracted four times with ether. The combined ether layers were washed with water until neutral and once with brine. Drying over $MgSO_4$ and evaporation of the solvent yielded 6.8 g of a yellowish oil containing 93% of the desired product. Distillation at ≈ 15 mm Hg resulted in 3.35 g (20 mmol; 47%) 4-methyl-5-phenylpent-1-ene (**15**) (bp 65°C; 96% pure as measured on GC). UV (cyclohexane): λ_{max} 260, 255, 250 nm. ^{1}H NMR (200 MHz): δ 7.28-7.11 (m, 5H, aromatic); 5.80 (dddd, 1H, H2, J=17.5, 9.5, 6.9, 7.2); 5.06-4.95 (double m, 2H, H1); 2.65 (dd, 1H, H5a, J=13.4, 5.8); 2.37 (dd, 1H, H5b, J=13.4, 7.6); 2.12 (br ddd, 1H, H3a, J=13.5, 5.5, 6.7); 1.92 (dtt, 1H, H3b, J=13.7, 2x7.2, 2x1.0); 1.81 (m, 1H, H4); 0.86 (d, 3H, CH_3, J=6.5). ^{13}C (50 MHz): δ 141.3 (quat. aromatic); 137.3 (C2); 129.2/128.1/125.7 (aromatic); 115.90 (C1); 43.2 (C5); 41.0 (C3); 35.0 (C4); 19.2 (CH_3).

4,4-Dimethyl-5-phenylpent-1-ene (16)

2,2-Dimethyl-1-phenylpent-4-en-1-one (VIb): A mixture of 5.0 g (34 mmol) isobutyrophenone, 4.4 g (36 mmol) allyl bromide and 7.5 g (67 mmol) potassium t-butoxide in 50 ml t-butyl alcohol was refluxed for 2.5 hours. After cooling, 50 ml water was added and the water layer was extracted twice with 50 ml ether. Drying over $MgSO_4$ and removal of the solvent yielded 5.3 g of oil of which still 12% was starting material (O-alkylation followed by hydrolysis during work-up!). Refluxing for another two hours with 1.5 g potassium t-butoxide and 1 ml allyl bromide yielded after work-up 5.25 g (28 mmol; 82%) 2,2-dimethyl-1-phenylpent-4-en-1-one (VIb) (97% pure as measured on GC). ^{1}H NMR (60 MHz): δ 7.8-7.3 (br m, 5H, aromatic); 5.7 (m, 1H, H2); 5.2-4.9 (m, 2H, H1); 2.5 (d, 2H, H3, J=7); 1.3 (s, 6H, CH_3).

4,4-Dimethyl-5-phenylpent-1-ene (16): Ketone VIb was reduced by means of a modification of the Wolff-Kishner reaction [33]. A suspension of 5.25 g ketone, 2.8 g hydrazine hydrate (99%) and 3.3 g potassium hydroxide was refluxed during ten hours. After cooling to room temperature 50 ml water and 25 ml pentane were added. The organic layer was washed with sodium bicarbonate, water and brine. Removal of the solvent yielded 4.15 g crude product (70% conversion). Column chromatography of 2.5 g crude product over silicagel (eluent: petroleum ether 40/60) yielded, after rigorous evaporation on the Rotavap at 70 °C, 0.70 g of the desired alkene with a purity of 94% as measured on GC. It was still contaminated with 4% isobutylbenzene (as judged from the retention time on GC) and 2% 4,4-dimethyl-5-phenylpent-2-ene (isolated with preparative GC). This mixture was irradiated as such. UV (cyclohexane): λ_{max} 265, 259, 254 nm. ^{1}H NMR (300 MHz): δ 7.29-7.17 (m, 3H, para and meta aromatic); 7.15-7.12 (br d, 2H, ortho aromatic, J=6.5); 5.89 (ddt, 1H, H2, J=16.7, 10.2, 2x7.4); 5.06 (br d, 1H, H1E, J=10.2); 5.03 (br d, 1H, H1Z, J=16.7); 2.51 (s, 2H, H5); 1.99 (br d, 2H, H3, J=7.4); 0.86 (s, 6H, both CH_3). ^{13}C NMR (50 MHz): δ 135.7 (C2); 130.7/127.7/125.8 (aromatic); 117.1 (C1); 48.4/46.7 (C5/C3); 34.3 (C4); 26.5 (both CH_3); quat. aromatic carbon atoms not visible.

4-Benzyl-5-methylhex-1-ene (17)

1-Phenyl-3-methylbutan-1-one (isovalerophenone; V): 13.5 g (83 mmol) Iron(III) chloride was suspended in 50 ml dry benzene[33]. Subsequently 10 ml (9.9 g; 82 mmol) 3-methylbutyryl chloride was added dropwise and the mixture was heated at 65 - 70°C until no more hydrogen chloride evolved. After cooling to room temperature 50 ml water and 50 ml ether were added. The organic layer was washed with water, 10% sodium carbonate solution and again with water. After washing with brine, drying over $MgSO_4$ and evaporation of the solvent 11.5 g of black oil remained. Distillation of this oil yielded 9.4 g (58 mmol; 71%) 1-phenyl-3-methylbutan-1-one (bp 77°C at 0.6 mm Hg) as a colourless liquid. ^{1}H NMR (60 MHz): δ 8.2-8.0 (m, 2H, ortho aromatic); 7.7-7.4 (m, 3H, meta and para aromatic); 2.85 (d, 2H, H2, J=6.5); 2.3 (m, 1H, H3); 1.0 (d, 6H, CH_3, J=7).

1-Phenyl-2-isopropylpent-4-en-1-one (VIc): To 9.4 g (58 mmol) of V in 40 ml dry THF was added 3.5 g of a dispersion of sodium hydride in oil (60% w/w). This mixture was refluxed for two hours. After cooling of the mixture, 7.2 g (59 mmol) allyl bromide was added dropwise. After another hour of reflux 50 ml water was added. Extraction of the water layer with ether, washing the combined organic layers with water, drying over $MgSO_4$ and evaporation of the solvent yielded 11.85 g (102%) of VIc as a yellow liquid, which still contained some water (NMR) and some diallylated product (GC). The liquid becomes more viscous upon standing. ^{1}H NMR (200 MHz): δ 7.98-7.85 (m, 2H, aromatic); 7.62-7.43 (m, 3H, aromatic); 5.71 (ddt, 1H, H4, J=16.9, 9.9, 2x6.8); 5.01 (dq, H5Z, J=16.9, 3x1.5); 4.90 (br d, H5E, J=9.9); 3.35 (ddd, 1H, H2, J=10.0, 6.5, 3.9); 2.58 (m, 1H, H3a); 2.34 (m, 1H, H3b); 2.07 (octet, 1H, C<u>H</u>$(CH_3)_2$, J≈6.7); 0.96 (d, 3H, CH_3, J=7.0); 0.94 (d, 3H, CH_3, J=7.0). IR (liquid film): 3060, 2920, 1670 cm^{-1}.

4-Benzyl-5-methylhex-1-ene (17): Analogously to the synthesis of **15** 2.0 g (9.9 mmol) of VIc, 1.0 g (20 mmol) hydrazine hydrate and 0.9 g (16 mmol) potassium hydroxide in 20 ml diethylene glycol were refluxed overnight. After cooling 30 ml water and 25 ml hexane were added. The organic layer was washed with water until neutral and once with brine. Drying over $MgSO_4$ and evaporation of the solvent afforded 1.6 g of a yellow oil. Purification over silicagel in petroleum ether yielded 300 mg (1.6 mmol; 16%) 4-benzyl-5-methylhex-1-ene (**17**) with a purity of 87% as measured on GC; 8% 4-benzyl-5-methylhex-2-ene[34] as major contamination (NMR). ^{1}H NMR (200 MHz): δ 7.29-7.11 (m, 5H, aromatic); 5.74 (m, 1H, H2); 5.03-4.95 (double m, 2H, H1, J≈16, 10); 2.60 (dd, 1H, H1'a, J=13.7, 6.5); 2.45 (dd, 1H, H1'b, J=13.7, 7.6); 2.06 (br dt, 1H, H3a, J=14.1, 2x6.8); 1.93 (br dt, 1H, H3b, J=14.1, 2x7.1); 1.74 (m, 1H, H4); 1.60 (m, 1H, H5); 0.92 (d, 3H, H6 or CH_3, J=6.9); 0.88 (d, 3H, H6 or CH_3, J=6.9). ^{13}C NMR (50 MHz): δ 142.0 (quat. aromatic); 138.1 (C2); 129.2/128.2 (ortho and meta aromatic); 125.6 (para aromatic); 115.6 (C1); 46.0 (C4); 36.9 (C1'); 34.6 (C3); 28.8 (C5); 19.2/18.9 (both CH_3).

2-Allyl-2-benzyltetrahydrofuran (18)

2-Benzylidenetetrahydrofuran (VII): The synthesis was carried out according to the synthesis of the para fluoro compound described by Coppola[35]. To a solution of 6.1 g (87 mmol) 2,3-dihydrofuran in 120 ml THF at 0°C was added dropwise 54 ml 1.6 M n-BuLi (in hexane) under nitrogen. The yellow solution was stirred for two hours at 0°C. Subsequently 13.5 g (79 mmol) benzyl bromide was added dropwise and the solution was stirred for one hour at 0°C. After having been stirred overnight at room temperature the orange solution was mixed with 150 ml water. The water layer was extracted twice with 100 ml ether and the combined ether layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent yielded 12.5 g of an orange liquid, which after distillation at reduced pressure yielded 5.3 g (31 mmol; 39%) of colourless 2-benzylidenetetrahydrofuran (VII) (bp 104-105°C at 0.6 mm Hg), which colours very fast. ^{1}H NMR (60 MHz): δ 7.7-7.1 (br m, 5H, aromatic); 5.3 (s, 1H, H1'); 4.3 (t, 2H, H5, J=7); 2.7 (t, 2H, H3, J=7); 1.95 (quin, 2H, H4, J=7). UV(cyclohexane): λ_{max} 269 nm.

5-Hydroxy-1-phenylpentan-2-one (VIII): To 5.3 g (31 mmol) 2-benzylidenetetrahydrofuran (VII) in 130 ml THF 10 ml water and 2 ml concentrated hydrochloric acid were added and the mixture was stirred for four hours[35]. The solution was neutralized with 10 g sodium carbonate in 60 ml water. The organic layer was separated and the water layer twice extracted with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent yielded 5.35 g (30 mmol; 97%) of a yellow oil (mixture of the hemiketal and γ-hydroxyketone). ^{1}H NMR (200 MHz): γ-Hydroxyketone: δ 7.24 (m, 5H, aromatic); 3.65 (s, 2H, H1); 3.50 (t, 2H, H5, J=7); 2.50 (t, 2H, H3, J=7.1); 1.85-1.71 (m, 2H, H4). Hemiketal: δ 7.24 (m, 5H, aromatic); 3.76 (m, 2H, H5); 2.99 (s, 2H, H1'); 2.02-1.6 (m, 4H, H3, H4). IR (liquid film): 3450, 2925, 1700 cm^{-1}.

2-Benzyl-2-methoxytetrahydrofuran (IX): To 2.0 g (11 mmol) hydroxyketone VIII in 25 ml methanol were added a few granules of molsieve and three drops of concentrated sulfuric acid. The mixture was stirred for four days at room temperature and the reaction was subsequently quenched with 3 g sodium carbonate in 25 ml water. The methanol-water mixture was extracted with ether and the combined ether layers were washed with brine and dried over $MgSO_4$. Removal of the solvent yielded 1.85 g (9.6 mmol; 87%) 2-benzyl-2-methoxytetrahydrofuran (IX). ^{1}H NMR (200 MHz): δ 7.25-7.11 (m, 5H, aromatic); 3.78 (m, 2H, H5); 3.29 (s, 3H, OCH_3); 3.07 (d, 1H, H1''a, J=13.7); 2.97 (d, 1H, H1''b, J=14.0); 2.02-1.58 (m, 4H, H3+H4).

2-Allyl-2-benzyltetrahydrofuran (18): Analogous to compound **13** 1.70 g (8.9 mmol) 2-benzyl-2-methoxytetrahydrofuran (IX), 3.0 g (13.3 mmol) zinc bromide and 2.3 g (20 mmol) allyltrimethylsilane in 50 ml dichloromethane were stirred for 24 hours. Work-up resulted in 1.35 g product, which was purified by means of silica chromatography (eluent: 2% ether in petroleum ether 40/60) yielding 0.95 g (4.7 mmol; 53%; 99% pure) 2-allyl-2-benzyltetrahydrofuran (**18**). ^{1}H NMR (200 MHz): δ 7.28-7.19 (m, 5H, aromatic); 5.89 (ddt, 1H, H2'', J=16.5, 10.6, 2x7.2); 5.20-5.02 (double m, 2H, H3''); 3.77 (m, 2H, H5); 2.82 (d, 1H, H1'a, J=13.7); 2.73 (d, 1H, H1'b, J=13.7); 2.26 (dd, 2H, H1''a/H1''b, J=7.2, 1.0); 1.81-1.52 (m, 4H, H3/H4). ^{13}C NMR (50 MHz): δ 138.2 (quat. aromatic); 134.7 (C2''); 130.5/127.8/126.0 (aromatic); 117.7 (C3''); 84.6 (C2); 67.9 (C5); 45.0/44.1 (C1'/C1''); 33.5/26.1 (C3/C4). IR (liquid film): 2920, 2850, 1040 cm^{-1}.

Irradiation, purification and characterization

Table 10 Irradiation, detection and isolation conditions.

comp.	st. mat. (mg)	irr. time (h)	conv. (%)	column AGC[a]	T_{col} (°C)	column PGC[d]	T_{col} (°C)
10	225	11	85	A	110		
11	300	8	92	B	120		
12	135	8	84	B	135[b]		
13	205	8.5	92	A	110		
14	200	14	97	A	130	A	150
15	200	11	97	B	105	B	120
16	205	9	85	A	110	A	115[e]
17	200	9	>79	B	120	B	135
18	200	10	79	B	130[c]		

[a] column A: Varian 3400 GC (OV101, 25m, carrier gas H_2); column B: Hewlett Packard 5700A GC (OV17, 50m, carrier gas H_2)

[b] 4 minutes at 135°C and subsequently with 8°/min to 200°C

[c] 8 minutes at 130°C and subsequently with 8°/min to 200°C

[d] Varian Aerograph model 90P, carrier gas H_2; column A: 15% Carbowax on Chromosorb WAW, 45-60μ, 6mx8mm; column B: 15% SE30 on Chromosorb WAW, 45-60μ, 6mx8mm

[e] after 30 minutes at 115°C the temperature was raised to 170°C to shorten the run

Table 11 Isolation conditions for preparative HPLC and relative retention times (rrt) of the products with respect to the starting material.

		rrt of each type of adduct					
comp.	eluent[a]	**ax**	**ay**	**bx**	**by**	**cx**	**cy**
10	A	2.20	2.29		2.77	2.01	3.51
11	B	2.47	1.69	2.01	2.28	1.38	
12	C			3.18			
13	D	2.33	1.13		1.34	0.91	1.61
18	E		1.36	1.82	2.06	0.74	1.98

[a] A = 0.6% 2-methyl-2-butanol/15% diethyl ether in hexane; B = 1.5% 2-methyl-2-butanol/10% diethyl ether in hexane; C = 10% diethyl ether in hexane; D = 5% diethyl ether in hexane; E = 1.7% diethyl ether in hexane

Table 12 Meta-adducts (relative retention times on AGC) formed by the irradiation of compounds **10** - **18**.

Compound: meta-adduct: retention time relative to starting material (percentage); other products: (o.p.): retention time relative to starting material (percentage).	
10	**10dx**: 0.88 (7%); **10dy**: 0.98 (5%); **10ay**: 1.22 (15%); **10ax**: 1.29 (6%); **10bx**: 1.31 (4%); **10by**: 1.32 (12%); **10cx**: 1.42 (14%); **10cy**: 1.49 (18%).
11	**11dx**: 0.78 (1%); **11ay**: 0.99 (13%); **11bx**: 1.03 (27%); **11by**: 1.06 (6%); **11ax**: 1.07 (35%); **11cx**: 1.14 (6%); o.p.: 1.15 (2%); 1.21 (1%); 1.29 (2%).
12	**12ax**: 1.04 (41%); **12bx**: 1.05 (42%); o.p.: 1.02 (3%).
13	**13ay**: 1.20 (14%); **13by**: 1.27 (16%); **13cx**: 1.31 (22%); **13cy**: 1.37 (30%); o.p.: 0.95 (1%).
14	OV101: **14ay**: 0.93 (35%); **14bx**: 0.99 (13%); **14ax** and **14by**: 1.00 (34%); o.p.: 0.81 (1%), 0.85 (1%), 1.08 (9%), 1.23 (5%). Carbowax (15% on Chromosorb WAW, 25m): (3% starting material left) **14ay**: 0.78 (33%); **14bx**: 0.89 (10%); **14ax** and **14by**: 0.94 (36%); o.p.: 1.20 (8%), 1.30 (5%).
15	**15dy**: 0.67 (2%); **15dx**: 0.76 (3%); **15a** and **15b**: 0.88 (20%); **15cy**: 1.03 (31%); **15cx**: 1.08 (35%); o.p.: 0.95 (4%).
16	**16a**: 0.80 (32%); **16b**: 0.82 (37%); o.p.: 1.09 (2%), 1.32 (3%); contaminations from starting material: 0.90 (5%) and 1.04 (2%).
17	**17dy**: 0.86 (3%); **17dx**: 0.92 (4%); **17a** or **17b**: 1.00 (21%) or 1.05 (5%); **17cy**: 1.10 (21%); **17cx**: 1.12 (25%); contamination from starting material: 0.97 (10%).
18	OV17: **18ay**: 1.01 (28%); **18bx**: 1.05 (11%); **18by**: 1.06 (18%); **18cx**: 1.07 (7%); **18ax**: 1.08 (6%); **18cy**: 1.13 (3%); o.p.: 1.10 (1%; no meta-adduct), 1.15 (2%). OV101: **18ay**: 1.12 (26%); **18bx** and **18by**: 1.22 (26%); **18cx** and **18ax**: 1.28 (15%); **18cy**: 1.48 (9%); o.p.: 1.04 (1%), 1.07 (1%), 1.35 (2%), 1.40 (1%).

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[36]. 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 1a-d.

*10-endo-Hydroxytetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**10ax**):* (isolated within fraction of **10by**).

*10-exo-Hydroxytetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**10ay**):* (85%, 7% starting material) ^{13}C NMR (75.5 MHz): δ 133.3 (C5); 128.5 (C4); 76.3 (C10); 51.7 (C6); 49.5/41.0 (2x) (C7, C9, C11); 42.3/38.8/35.1 (C2, C3, C8); quaternary C not visible.

*10-exo-Hydroxytetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**10by**):* (73% together with 17% **10ax** and 6% **10cy**) ^{1}H NMR NOE: H2: (H11a).

*3-endo-Hydroxytetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**10cx**):* (95% pure) ^{1}H NMR NOE: H3: (H2b, H4b, H11). ^{13}C NMR (75.5 MHz): δ 129.7/129.4 (C9 + C10); 69.2 (C3); 57.7/50.8 (C5, C11); 42.6/41.9 (C2 + C4); 39.8/25.8 (C7,C8); 27.8 (C6); quaternary C not visible.

*3-endo-Hydroxytetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**10cy**):* (93% pure) ^{1}H NMR NOE: H3: (H7); H7: (H8, H3). ^{13}C NMR (75.5 MHz): δ 129.3/128.9 (C9 + C10); 70.7 (C3); 59.0/51.6 (C5, C11); 43.0/41.0 (C2, C4); 40.4/25.7 (C7, C8); 27.7 (C6); quaternary C not visible.

*10-endo-Hydroxy-10-exo-methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**11ax**):* (98% pure) ^{1}H NMR NOE: H8 (H9a); H9a (H11a/H9b/H8); H9b (H8/H9a/CH_3); CH_3 (-). ^{13}C NMR (75.5 MHz): δ 133.50 (C5); 128.28 (C4); 82.12 (C10); 52.11 (C6); 48.13 (C7); 47.50 (C9); 46.60 (C11); 46.24 (C1); 41.26 (C2); 39.74 (C8); 36.89 (C3); 28.33 (CH_3). MS m/z (%): 176 (17), 161 (13), 158 (100), 143 (58), 133 (61), 128 (19), 118 (80), 117 (43), 115 (30), 105 (25), 93 (18), 92 (20), 91 (54), 79 (13), 77 (18), 66 (21), 51 (10), exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1198.

Eu(FOD)$_3$ complex of **11ax**: ^{1}H NMR: δ 5.94 (H4); 5.76 (H5); 5.43 (H9a); 5.25 (H11a); 4.38 (CH_3); 4.06 (H8); 3.97 (H11b); 3.83 (H9b); 3.77 (H6); 3.16 (H2); 2.83 (H7b); 2.65 (H3); 2.48 (H7a).

*10-exo-Hydroxy-10-endo-methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**11ay**):* (94% pure) ^{1}H NMR NOE: H2 (H3). ^{13}C NMR (75.5 MHz): δ 133.25 (C5); 128.37 (C4); 82.06 (C10); 51.27 (C6); 49.05 (C7); 46.81 (C1); 46.32 (C11); 45.91 (C9); 42.05 (C2); 39.53 (C8); 34.73 (C3); 27.69 (CH_3). MS m/z (%): 176 (3), 159 (8), 158 (100), 143 (75), 133 (25), 118 (35), 117 (77), 115 (30), 103 (19), 92 (35), 91 (49), 77 (24), 65 (15), 51 (10), exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1196.

Eu(FOD)$_3$ complex of **11ay**: ^{1}H NMR: δ 7.2 (CH_3); 6.53 (H4); 6.05 (H5); 5.65 (H9b); 5.57 (H11b); 4.71 (H8); 4.57 (H7b); 4.23 (H2); 3.78 (H6); 3.37 (H3); 2.99 (H7a).

*10-endo-Hydroxy-10-exo-methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**11bx**):* (85% together with 7% **11ax**) ^{1}H NMR NOE: H2 (H11); H8 (H11/H9a or b); H5 (H11/H6); H11(a+b) (H2/H5/CH_3); CH_3 (H9a or b/ H11). ^{13}C NMR (75.5 MHz): δ 137.08 (C2); 125.40 (C3); 81.64 (C10); 59.47 (C8); 49.54 (C11); 47.17 (C9); 42.97 (C5); 32.73 (C4); 30.30 (CH_3); 30.21 (C6); 27.07 (C7); quaternary C1 not visible. MS m/z (%): 176 (10), 159 (4), 143 (16), 133 (13), 128 (16), 117 (63),

115 (42), 105 (23), 92 (100), 91 (83), 85 (21), 79 (28), 77 (43), 65 (32), 57 (15), 55 (13), 51 (36), exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1204.

Eu(FOD)$_3$ complex of **11bx**: ^{1}H NMR: δ 6.35 (H2); 5.97 (H11a); 5.95 (H3); 5.4(H9a); 5.31 (H8); 4.80 (CH_3); 4.30 (H11b); 3.91 (H9b); 3.50 (H5); 2.54 (H7b); 2.45 (H7a); 2.39 (H6); 2.38 (H4).

Trimethylsilyl derivative of **11bx**: ^{1}H NMR: δ 5.50 (dd, H3, J(3,2) = 5.3, J(3,4) = 2.2); 5.41 (br d, H2, J(2,3) = 5.3); 2.43 (dt (app. as quintet), H8, J(8,9b) = 12.0, J(8,9a) = J(8,7a) = 6.0); 2.23 (dd (app. as t), H5, J(5,4) = 6.7, J(5,6) = 6.2); 2.08 (dd, H11a, J(11a,11b) = 14.3, J(11a,9a) = 1.1); 1.92 (d, H11b, J(11b,11a) = 14.3); 1.78 (dt, H4, J(4,5) = J(4,6) = 6.7, J(4,3) = 2.2); 1.75 - 1.6 (m, H6, H7, H9); 1.42 (s, CH_3); 0.08 (s, $OSiCH_3$). NOE: H8 (-); H5 (H11b); H11a (H2/H11b/Si$\underline{CH}_3$); H11b (H5/H11a); CH_3 (H11b/H9b); OSi$\underline{CH}_3$ (CH_3). ^{13}C NMR (75.5 MHz): δ 137.45 (C2); 125.08 (C3); 59.63 (C8); 50.67 (C11); 47.83 (C9); 43.10 (C5); 32.63 (C4); 30.69 (CH_3); 30.30 (C6); 27.04 (C7); 2.41 (OSi$\underline{CH}_3$); quaternary C's not visible.

*10-exo-Hydroxy-10-endo-methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**11by**):* (97% pure) ^{1}H NMR NOE: H2 (H11a); H5 (H11b/H9b); H8(+H11b) (-); CH_3 (H11a/H8/H9a). ^{13}C NMR (75.5 MHz): δ 136.76 (C2); 125.67 (C3); 80.73 (C10); 67.02 (C1); 59.42 (C8); 49.06 (C11); 47.47 (C9); 42.85 (C5); 33.09 (C4); 31.02 (CH_3); 30.03 (C6); 27.67 (C7). MS m/z (%): 176 (1), 159 (12), 158 (58), 143 (100), 133 (13), 128 (22), 117 (42), 115 (25), 103 (48), 93 (20), 92 (36), 91 (49), 77 (17), 65 (10), 51 (8), exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1199.

Eu(FOD)$_3$ complex of **11by**: ^{1}H NMR: δ 5.74 (H2 + H3); 3.82 (H11b); 3.74 (H9b); 3.34 (H5); 3.08 (H11a); 3.06 (H9a); 2.88 (CH_3); 2.86 (H8); 2.13 (H7a); 2.11 (H4); 2.02 (H6); 2.00 (H7b).

Trimethylsilyl derivative of **11by**: ^{1}H NMR: δ 5.50 (ddd, H3, J(3,2) =5.3, J(3,4) = 2.4); 5.30 (br d, H2, J(2,3) = 5.3); 2.49 (br dd (app. as t), H5, J(5,4) = 7.0, J(5,6) = 6.1); 2.09 (d, H11b, J(11b,11a) = 14.0); 1.90 (d, H11a, J(11a,11b) = 14.0); 1.81 (br dt, H4, J(4,5) = 7.0, J(4,6) = 6.7, J(4,3) = 2.4); 2.05 - 1.95 and 1.75 - 1.65 (m, H6 - H9); 1.28 (s, CH_3); 0.14 (s, $OSiCH_3$). NOE: H2: (H3, H11a); H5: (H11b, H4); H11b: (H5, H11a); H11a: (H2, H11b); CH_3: (H11a); $OSiCH_3$: (H11b). ^{13}C NMR (75.5 MHz): δ 137.1 (C2); 125.5 (C3); 58.9 (C8); 50.0 (C11); 48.0 (C9); 43.5 (C5); 33.0 (C4); 31.5 (CH_3); 30.1 (C6); 27.7 (C7); 2.5 ($OSiCH_3$); quaternary C's not visible.

*3-endo-Hydroxy-3-exo-methyltetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**11cx**):* (75% together with 25% of starting material) ^{1}H NMR NOE: H2b(+H8): (H2a); H11: (-); H6b(+H4+H2a) (H5/H2b/H6a). MS m/z (%): 176 (1), 161 (4), 143 (25), 133 (13), 128 (18), 117 (100), 115 (51), 103 (22), 92 (46), 91 (84), 85 (11), 79 (26), 77 (42), 65 (34), 57 (11), 51 (36), exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1206.

*10-endo-Hydroxy-10-exo-isopropyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**12ax**):* (98% pure) ^{1}H NMR NOE: H11b: (H11a, both CH_3); H9a: (H9b, H8). ^{13}C NMR (75.5 MHz): δ 133.5 (C5); 128.2 (C4); 88.8 (C10); 53.5 (C6); 47.8/45.3/43.9 (C7, C9, C11); 40.9/40.6/38.7/36.7 (C2, C3, C8, C1'); 17.5 (both CH_3); quaternary C1 not visible.

*10-endo-Hydroxy-10-exo-isopropyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**12bx**):* (96% pure) ^{1}H NMR NOE: H8: (H9a); H5: (H11b, H4, H6); H11b: (H5, H11a, CH_3 at 0.97); H9a: (H9b, H8, CH_3 at 0.95); CH_3: (H1, H9a, H11b). ^{13}C NMR (75.5 MHz): δ 137.4 (C2); 125.3 (C3); 87.1 (C10); 59.0 (C8); 46.8/43.9 (C9, C11); 43.2/38.1/32.8/30.3 (C4, C5, C6, C1'); 27.2 (C7); 17.5 (both CH_3); quaternary C1 not visible.

*10-exo-Methoxytetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**13ay**):* (90% + 5% **13**) ^{13}C NMR (75.5 MHz): δ 133.3 (C5); 128.5 (C4); 84.7 (C10); 56.4/51.8 (C6, OCH_3); 48.8/37.2 (2x) (C7, C9, C11); 42.1/38.7/35.7 (C2, C3, C8); quaternary C not visible. MS: Exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1165.

*10-exo-Methoxytetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**13by**):* (88% + 7% **13ay**) ^{1}H NMR NOE: H10: (H11a, OCH_3); H5: (OCH_3, H4, H6). ^{13}C NMR (75.5 MHz): δ 136.6 (C2); 125.5 (C3); 83.4 (C10); 58.3/56.9 (C8, OCH_3); 42.2 (C5); 38.9/37.9 (C9, C11); 33.2/29.9 (C4, C6); 27.6 (C7); quaternary C not visible. MS: Exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1166.

*3-endo-Methoxytetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**13cx**):* (98% pure) ^{1}H NMR NOE: H3: (OCH_3, H2b, H11, H2a + H4?). ^{13}C NMR (75.5 MHz): δ 129.7/129.6 (C9, C10); 78.5 (C3); 57.7/56.3 (C11, OCH_3); 50.8 (C5); 40.2 (C8); 38.8/37.2 (C2, C4); 27.9 (C6); 26.3 (C7); quaternary C not visible. MS: Exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1172.

*3-exo-Methoxytetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**13cy**):* (95% pure) ^{1}H NMR NOE: H3: (OCH_3, H2a, H4a, H7); OCH_3: (H3, H2a, H2b, H4a); H2a (+ H11 + H4a): (H2b, H3, H7); H7: (H3, H8). ^{13}C NMR (75.5 MHz): δ 129.5/128.8 (C9, C10); 79.2 (C3); 58.9/56.4 (C11, OCH_3); 51.5 (C5); 40.3 (C8); 39.5/37.5 (C2, C4); 27.7 (C6); 25.3 (C7); quaternary C not visible. MS: Exact mass calculated for $C_{12}H_{16}O$ 176.1201, found 176.1171.

*10-endo-Methoxy-10-exo-methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-2-ene (**14ax**):* (see **14by**)

*10-exo-Methoxy-10-endo-methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-2-ene (**14ay**):* (90% pure) ^{1}H NMR NOE: OCH_3 + H6: (H11b, H2, H7b, CH_3); H2: (H11b); H8: (CH_3); CH_3: (H9a, H11a, OCH_3). ^{13}C NMR (75.5 MHz): δ 133.3 (C5); 128.4 (C4); 86.2 (C10); 51.8/50.1 (C6, OCH_3); 48.1/42.6/42.3 (C7, C9, C11); 41.7/39.5/35.7 (C2, C3, C8); 22.6 (CH_3); C1 not visible.

*10-endo-Methoxy-10-exo-methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**14bx**):* (75% + 12% of an unknown product with 2 vinylic protons between 5.6 - 5.8 ppm) ^{1}H NMR NOE: OCH_3: (H11a, CH_3); H11a: (H11b, OCH_3, weak H2); CH_3:

(OCH_3, H11b, H9b). ^{13}C NMR (75.5 MHz): δ 137.1 (C2); 125.3 (C3); 59.4 (OCH_3); 49.6/42.9 (C5, C8); 32.8/30.2 (C4, C6); 46.3/42.6 (C9, C11); 27.2 (C7); 25.1 (CH_3); C1 not visible.

*10-exo-Methoxy-10-endo-methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**14by**):* (**14by** : **14ax** = 5 : 1) ^1H NMR NOE: OCH_3: (H11b, H9b, H11a, CH_3); H5: (H11b); CH_3: (OCH_3, H11a, H9a). ^{13}C NMR (75.5 MHz): δ 136.9 (C2); 125.7 (C3); 58.7/50.6/43.0 (C5, C8, OCH_3); 45.1/43.8 (C9, C11); 33.1/30.0 (C4, C6); 27.6 (C7); 25.9 (CH_3); quaternary C not visible.

*10-Methyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**15a**):* (isolated together with **15b**, **15** and both rearranged 2,6 in a ratio of 1.4 : 1.7 : 0.8 : 0.5).

*10-Methyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**15b**):* (see **15a**).

*8-endo-Methyltricyclo[4.3.2.0^{1,5}]undeca-2,10-diene (**15dx**):* (95% pure) ^1H NMR NOE: H9a: (H9b, CH_3); H7a: (H7b, H6, CH_3 (weak)); CH_3: (H8, H7a, H7b, H9a, H9b). ^{13}C NMR (50 MHz): δ 136.0/133.0/132.4/131.8 (C2, C3, C10, C11); 59.9 (C1); 59.3 (C5); 42.1 (C6); 37.5/35.6/34.6 (C4, C7, C9); 27.7/24.6 (C8, CH_3).

*8-exo-Methyltricyclo[4.3.2.0^{1,5}]undeca-2,10-diene (**15dy**):* (82% + 18% **15dx**) ^{13}C NMR (50 MHz): δ 135.8/133.0/129.4/128.6 (C2, C3, C10, C11); 62.2 (C5); 61.0 (C1); 42.8 (C6); 39.1/37.0/34.6 (C4, C7, C9); 26.3 (C8); 21.6 (CH_3).

*10,10-Dimethyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**16a**):* (92% pure) ^{13}C NMR (75.5 MHz): δ 133.26 (C5); 128.55 (C4); 52.29 (C6); 48.68/46.93/46.42 (C7, C9, C11); 41.81/40.96/36.38 (C2, C3, C8); 29.37 (CH_3); 29.19 (CH_3); quaternary C's not visible. MS m/z (%): 174 (32), 159 (38), 145 (4), 131 (42), 117 (96), 115 (50), 108 (61), 105 (33), 93 (66), 91 (92), 81 (37), 79 (47), 77 (60), 67 (100), 65 (44), 55 (56), 51 (42), exact mass calculated for $C_{13}H_{18}$ 174.1408, found 174.1411.

*10,10-Dimethyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**16b**):* (93% pure) ^{13}C NMR (75.5 MHz): δ 137.78 (C2); 124.92 (C3); 124.92 (C3); 59.83 (C8); 48.27/46.73 (C9, C11); 43.21 (C5); 32.68/29.89 (C4, C6); 31.93 (CH_3); 31.35 (CH_3); 27.47 (C7). MS m/z (%): 174 (1), 159 (17), 146 (4), 133 (24), 131 (31), 117 (68), 115 (40), 105 (19), 91 (90), 82 (24), 77 (33), 67 (35), 65 (34), 55 (100), 51 (25), exact mass calculated for $C_{13}H_{18}$ 174.1408, found 174.1402.

*8-Isopropyltetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**17a**):* (81% **17a** + **17b** (1 : 1.9), 5% **17dy**, 8% **17dx**, 4% **17**).

*8-Isopropyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-4-ene (**17b**):* (see **17a**).

*8-endo-Isopropyltricyclo[4.3.2.0^{1,5}]undeca-2,10-diene (**17dx**):* (1 : 1 mixture with 1-methyl-2-benzylpentane, also 4% **17**) ^{13}C NMR (75.5 MHz): δ 136.3* (C2); 132.8* (C3); 133.0/132.9 (C10, C11); 55.4 (C5); 45.6/33.9 (C8, C1'); 40.7 (C6); 37.1 (C9); 34.1 (C4); 30.6 (C7); 20.6/20.5 (both CH_3); quaternary C not visible.

*8-exo-Isopropyltricyclo[4.3.2.0^{1,5}]undeca-2,10-diene (**17dy**):* (92% + 6% **17dx**) ^1H NMR NOE: H5 + H7a: (H4b, H7b); H7a + H5: (H6, H7b, H11); H8 + H1': (H10, H11, CH_3, H7a + b, H9a + b); H7b + H9b: (H6, H7a, H9a, H5, H8). ^{13}C NMR (75.5 MHz): δ 135.9/133.0/129.2/128.7 (C2, C3, C10, C11); 61.5 (C5); 42.4/37.4/33.0 (C8, C6, C1'); 34.4/34.1/32.2 (C4, C7, C9); 20.5/20.2 (both CH_3); quaternary C not visible.

*(1SR,2RS,3SR,6RS,8RS,10RS)-Spiro[tetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene-10,2'-tetrahydrofuran] (**18ax**):* (93% pure) MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1350.

*(1SR,2RS,3SR,6RS,8RS,10SR)-Spiro[tetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene-10,2'-tetrahydrofuran] (**18ay**):* (92% pure) ^1H NMR NOE: H8: (H4, H7a, H9a); H9b + H11b: (H9a, H11a, H5', H2). ^{13}C NMR (75.5 MHz): δ 133.3 (C5); 128.5 (C4); 92.6 (C10); 66.9 (C5'); 51.5 (C6); 48.4/43.0/42.9/35.7/25.5 (C3', C4', C7, C9, C11); 42.2/39.3/35.6 (C2, C3, C8); C1 not visible. MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1361.

*(1RS,4SR,5SR,6SR,8SR,10SR)-Spiro[tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene-10,2'-tetrahydrofuran] (**18bx**):* (93% pure) ^1H NMR NOE: H2: (H11a); H5: (H11b); H11a: (H11b, H2). ^{13}C NMR (75.5 MHz): δ 137.0 (C2); 125.3 (C3); 66.3 (C5'); 56.7 (C8); 46.8/43.6 (C9,C11); 42.3 (C5); 37.8/29.7/27.2 (C7, C3', C4'); 32.8/30.1 (C4, C6); quaternary C's not visible. MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1348.

*(1RS,4SR,5SR,6SR,8SR,10RS)-Spiro[tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene-10,2'-tetrahydrofuran] (**18by**):* (48% + 24% **18cy** + 14% **18bx** + 8% **18ay**) ^1H NMR NOE: H2: (H11a); H5: (H11b). ^{13}C NMR (75.5 MHz): δ 136.7 (C2); 125.8 (C3); 66.8 (C5'); 59.0 (C8); 45.9/44.2/39.4 (C9, C11, C3'); 42.8 (C5); 33.0/30.1 (C4, C6); 27.7/25.6 (C7, C4'); quaternary C's not visible. MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1350.

*(1RS,3RS,5SR,7SR,8SR,11RS)-Spiro[tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene-3,2'-tetrahydrofuran] (**18cx**):* (57% + 17% **18** + 10% **18ay** + 8% **18by**) ^{13}C NMR (75.5 MHz): δ 129.6/129.5 (C9, C10); 66.2 (C5'); 58.9/51.8 (C5, C11); 45.8/44.2/40.4 (C2, C4, C3'); 40.6 (C8); 27.0/24.9 (C6, C4'); 25.5 (C7); quaternary C's not visible. MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1367.

*(1RS,3SR,5SR,7SR,8SR,11RS)-Spiro[tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene-3,2'-tetrahydrofuran] (**18cy**):* (93% pure) ^1H NMR NOE: H3'a: (H3'b, H7); H7: (H3'a, H8, H6b). ^{13}C NMR (75.5 MHz): δ 129.7/129.0 (C9, C10); 65.9 (C5'); 58.0/51.6 (C5, C11); 46.0/45.9/41.6 (C2, C4, C3'); 40.7 (C8); 27.4/25.8 (C6, C4'); 25.6 (C7); quaternary C's not visible. MS: Exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1365.

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