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PHOTOCHEMISTRY OF NON-CONJUGATED BICHROMOPHORIC SYSTEMS

FORMATION OF CUBANE-LIKE PHOTOCYCLOMERS IN DI-(α-NAPHTHYL) COMPOUNDS

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Abstract—Irradiation of di-(α-naphthylmethyl)ether I, [2-(α-naphthyl) ethyl]-(α-naphthylmethyl)ether II and 1,3-di-(α-naphthyl)propanol III, with wavelengths longer than 300 nm results finally for all of these compounds in the formation of "cubane-like" photocyclomers. The structures of these cyclomers were elucidated by ^{1}H-NMR-spectroscopy. A general scheme for "cubane-like" photocyclomerization in di-(α-naphthyl) compounds is proposed.

Photodimers of aromatic compounds have been known for over a century, but the first report of the isolation of a photodimer in the naphthalene series appeared in 1963,[1] with an article about the intermolecular $(4\Pi s + 4\Pi s)$ photodimerisation of β-methoxynaphthalene. Since then several intermolecular photodimerisations of naphthalene-derivatives have been reported,[2] in which as well *endo*-, *exo*- as "cubane-like" cyclomers were formed (Fig. 1).

In 1970, Chandross *et al.* discovered the first intramolecular $(4\Pi s + 4\Pi s)$-photocyclomerization in the naphthalene series, with the formation of *endo*- and *endo*-Cope-rearranged-cyclomers from 1,3-di-(α-naphthyl)-propane.

In this paper we report the results of a study of the photo-chemical behaviour of the non-conjugated bichromophoric compounds di-(α-naphthylmethyl)-ether I, [2-(α-naphthyl)ethyl]-(α-naphthylmethyl)-ether II and 1,3-di-(α-naphthyl)propanol III, in

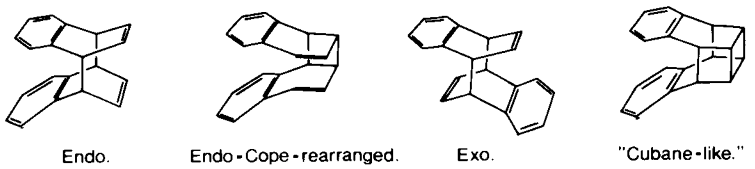
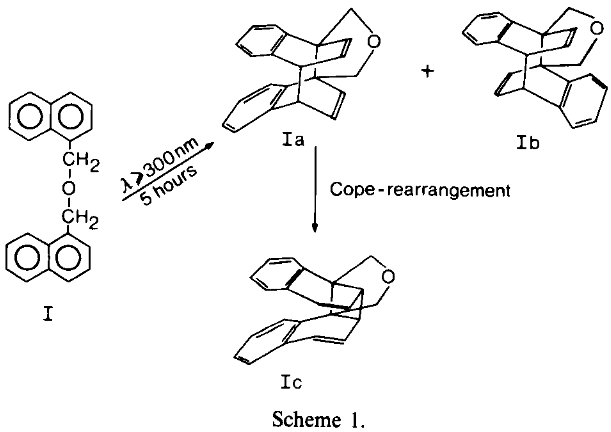


Fig. 1. Structure of dimers of naphthalene derivatives.



Scheme 1.

which intramolecular formation of "cubane-like" photocyclomers is observed.

RESULTS

Di-(α-naphthylmethyl)ether I. In a previous paper[4] we reported the formation of cyclomers I_a and I_b, by irradiation of iso-octane solutions of di-(α-naphthylmethyl)-ether I. Hereby I_a underwent thermal Cope-rearrangement to I_c (Scheme 1).

We now observed that irradiation of I, under the same conditions, but for longer times (Experimental) resulted in the formation of cyclomers I_b and I_d (Scheme 2), in the same ratio as I_b and I_a in the previous experiment. Moreover, irradiation of pure I_c for longer times resulted in quantitative conversion to I_d.

From the strongly coupled 360 MHz ^{1}H-NMR-spectrum of I_d, J-and δ-values (Table 1) for the non aromatic protons are obtained, using computer simulation (SIMEQ II), (Fig. 2). The arylprotons absorb at 7.0 ppm as a multiplet.

[2-(α-*Naphthyl)ethyl*] (α-*naphthylmethyl)ether* II. Prolonged irradiation of iso-octane solutions of [2-(α-naphthyl)ethyl]-(α-naphthylmethyl)ether II at room temperature yields compounds II_a and II_b (ratio 1/5) (Scheme 3).

The mass spectra of II_a and II_b show a molecular ion peak at *m/e* 312, proving the intramolecular character of the photoreaction. The presence of compound II_a is evidenced by the δ- and J-values of its olefinic and aromatic protons, which are fully comparable with those of the *endo*-Cope rearranged cyclomer I_c.

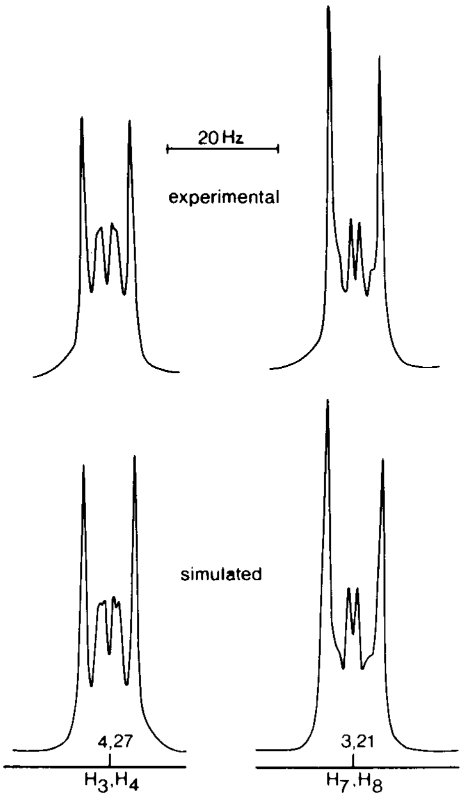
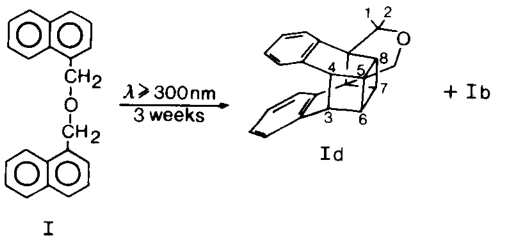
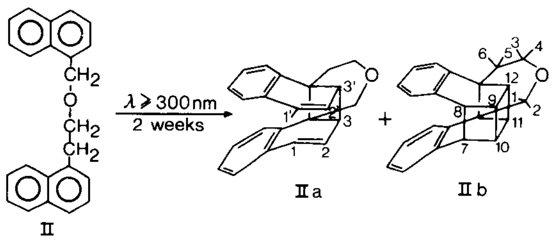


Fig. 2. ^{1}H-NMR signals of protons H_3, H_4, H_7 and H_8, simulated and experimentally obtained on a 360 MHz apparatus.



Scheme 2.



Scheme 3.

Table 1: ^{1}H-NMR data for I_d (CDCl$_3$/TMS); δ (underlined) in ppm and J in Hz

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8
H_1	4,63	-9,5	/	/	/	/	/	/
H_2		4,09	-9,5	/	/	/	/	/
H_3			4,27	11,1	0,9	8,2	0,2	0,0
H_4				4,27	8,2	0,9	0,0	0,2
H_5					3,21	6,4	1,5	8,1
H_6						3,21	8,1	1,5
H_7							2,89	7,2
H_8								2,89

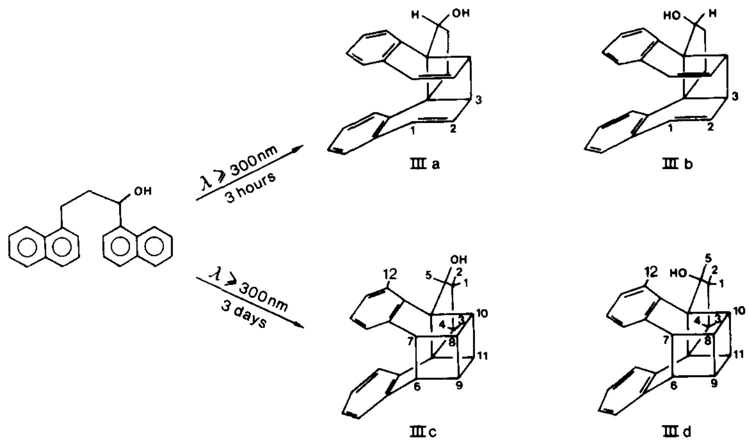
Aromatic protons: $\delta = 6{,}95$ ppm (m). Olefinic protons: H_1: $\delta = 6.32$ ppm ($J_{1,2} = 9.6$ Hz, $J_{1,3} = 0.8$ Hz.[5] H_2: $\delta = 5.80$ ppm ($J_{1,2} = 9.6$ Hz, $J_{2,3} = 3.6$ Hz). $H_{1'}$: $\delta = 6.20$ ppm ($J_{1',2'} = 9.6$ Hz, $J_{1',3'} = 1.6$ Hz.[5] $H_{2'}$: $\delta = 5.65$ ppm ($J_{1',2'} = 9.6$ Hz, $J_{2',3'} = 5.2$ Hz).

The strongly coupled 360 MHz-^{1}H-NMR spectrum of II_b was analyzed, using computer simulation (SIMEQ II) (Fig. 3). The coupling constants and chemical shifts obtained for the non-aromatic protons are summarized in Table 2. For the arylprotons a multiplet at 7.0 ppm is found. These J- and δ-values permit us to assign the structure depicted in Scheme 3 to II_b.

Protons H_1 and H_6 are highly deshielded as compared to respectively H_2 and H_5 ($\Delta\delta_{H_1H_2} = 1.20$ ppm), as one would expect from the anisotropy of the aromatic ring. From the vicinal coupling constant $^3J_{4,6}$(12.0 Hz) evidence can be found for the axial-axial position of protons H_4 and H_6.

1,3-Di(α-naphthyl)propanol III. Irradiation of 1,3-di-(α-naphthyl)propanol III,[6] in iso-octane at room temperature, up to 10% conversion results in the formation of III_a and III_b (ratio 1/9) which can by a prolonged irradiation be converted to III_c and III_d (Scheme 4).

The NMR-data (100 MHz-spectra, $CDCl_3$/TMS) of the aryl- and olefinic protons of III_a and III_b are fully comparable with those of the Cope rearranged product of the *endo*-cyclomer I_c of di-(α-naphthylmethyl)ether I. III_a: aromatic protons: $\delta = 7.0$ ppm (m). olefinic protons: $\delta_{H_1} = 6.15$ ppm ($J_{1,2} = 10$ Hz). $\delta_{H_2} = 5.65$ ppm ($J_{1,2} = 10$ Hz;



Scheme 4.

Table 2. ^{1}H-NMR data for II_b ($CDCl_3$/TMS); δ (underlined) in ppm and J in Hz

	H_1	H_2	H_3	H_4	H_5	H_6
H_1	$\underline{4{,}80}$	-11,4	0,0	0,0	0,0	0,0
H_2		$\underline{3{,}65}$	0,0	0,0	0,0	0,0
H_3			$\underline{4{,}33}$	-10,0	1,8	7,2
H_4				$\underline{4{,}41}$	4,7	12,0
H_5					$\underline{1{,}71}$	-14,0
H_6						$\underline{3{,}33}$

	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}
H_7	$\underline{4{,}22}$	11,8	0,9	7,5	0,3	0,0
H_8		$\underline{4{,}24}$	7,5	0,9	0,0	0,3
H_9			$\underline{3{,}24}$	7,0	1,5	7,0
H_{10}				$\underline{3{,}26}$	8,0	1,8
H_{11}					$\underline{3{,}39}$	7,0
H_{12}						$\underline{3{,}20}$

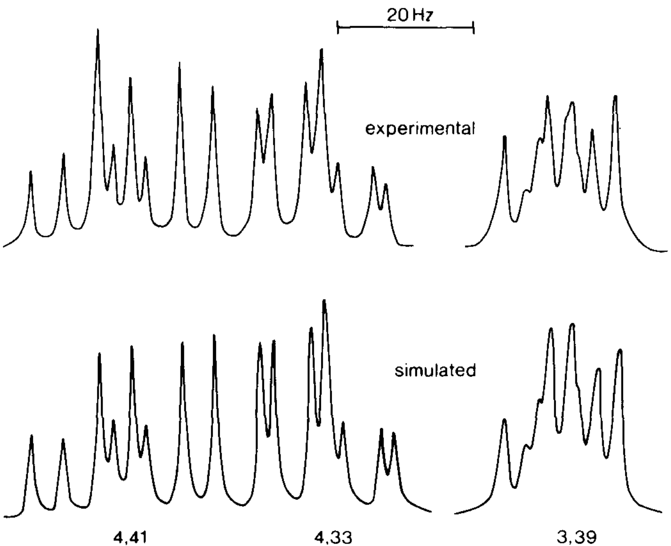


Fig. 3. ^{1}H-NMR signals of protons H_3, H_4 and H_{11}, simulated and experimentally obtained on a 360 MHz apparatus.

$J_{2,3} = 5.8$ Hz). III_b: aromatic protons: $\delta = 6.90$ ppm (m). olefinic protons: $\delta_{H_1} = 6.20$ ppm ($J_{1,2} = 9.8$ Hz). $\delta_{H_2} = 5.70$ ppm ($J_{1,2} = 9.8$ Hz; $J_{2,3} = 6.0$ Hz).

The stereochemical assignment of III_c and III_d was based on the J- and δ-values obtained from computersimulation of the strongly coupled 360 MHz NMR-spectra (Table 3).[6]

For the arylprotons, the following values were obtained: III_c: d at $\underline{7.23}$ (1 H, J = 7.5 Hz); d at $\underline{7.19}$ (1 H, J = 7.5 Hz) and multipled at ± 7.0 (6 H). III_d: dd at $\underline{8.46}$ (1 H, J = 7.5 Hz and J = 2.0 Hz); d at $\underline{7.34}$ (1 H, J = 7.5 Hz) and a multiplet at ± 7.0 (6 H).

Comparison of the ^{1}H NMR spectra shows that proton H_5 is highly deshielded in III_c ($\Delta\delta = 0.60$ ppm), as one would expect from the anisoptropy of the aromatic ring. On the other hand there is a striking difference between the peaks associated with the orthoaryl protons H_{12} in III_d and III_c. Inspection of Dreiding models indicates that H_{12} in III_d (8.46 ppm) should be deshielded as compared to

Table 3. ^{1}H-NMR data for III_c and III_d (CDCl$_3$/TMS); δ (underlined) in ppm and J in Hz

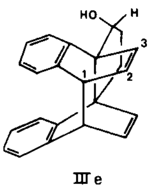
	III_c						III_d					
	H_1	H_2	H_3	H_4	H_5		H_1	H_2	H_3	H_4	H_5	
H_1	$\underline{2,20}$	-11,1	5,6	13,0	11,0		$\underline{2,54}$	-13,0	5,9	12,0	3,1	
H_2		$\underline{2,38}$	0,5	6,0	5,9			$\underline{2,03}$	1,2	6,0	1,4	
H_3			$\underline{1,65}$	-12,5	0,5				$\underline{1,71}$	-12,0	0,5	
H_4				$\underline{2,68}$	0,0					$\underline{3,17}$	0,7	
H_5					$\underline{5,08}$						$\underline{4,48}$	
	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_6	H_7	H_8	H_9	H_{10}	H_{11}
H_6	$\underline{4,25}$	13,0	0,0	7,6	0,0	0,0	$\underline{4,24}$	11,0	0,0	8,0	0,0	0,5
H_7		$\underline{4,25}$	7,6	0,0	0,0	0,0		$\underline{4,20}$	8,0	0,0	0,5	0,0
H_8			$\underline{3,26}$	7,1	6,9	1,8			$\underline{3,15}$	6,7	6,8	1,5
H_9				$\underline{3,24}$	1,8	6,9				$\underline{3,13}$	1,5	6,8
H_{10}					$\underline{3,11}$	6,8					$\underline{2,61}$	6,9
H_{11}						$\underline{2,70}$						$\underline{2,49}$

H_1 in III_c (7.23 ppm) due to its proximity to the OH-group.[2b] In the same way H_{10} in III_c (3.11 ppm) should be deshielded as compared to H_{10} in III_d (2.61 ppm). Furthermore, from the vicinal coupling constants $^3J_{1,4}$ (12.0 Hz in III_d and 13.0 Hz in III) evidence can be found for the axial–axial position of the protons H_1 and H_4 as well in III_d as in III_c. On this basis one can deduct from the vicinal coupling constants $^3J_{1,5}$ (3.1 Hz in III_d and 11.0 Hz in III_c) that the OH-group has an axial position in III_d and an equatorial one in III_c as depicted in Scheme 4. III_c and III_d show the following infrared absorption for the OH group: III_c: broad band between 3400 and 3100 cm^{-1}. III_d: 3575 (sharp, 11%); 3540 (sharp 30%); 3500–3300 (broad, 40%) 3400–3200 (broad, 13%).

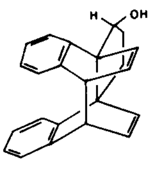
The bands at 3575 and 3540 cm^{-1} are characteristic for OH with intramolecular single bridge H-bond, or OH-π-association,[7] while those between 3500 and 3300 cm^{-1} can be attributed to OH with intermolecular dimeric bond[8] and those between 3400 and 3200 cm^{-1} to OH with intermolecular polymeric H-bond.[9]

The OH-π interaction, which occurs in III_d, but which is totally absent in isomer III_c, could be an explanation for the fact that III_c and III_d are formed in a ratio 1/9.

To check if (4Πs + 4Πs) cyclo-adducts are formed, which could not be detected after working up at room temperature, the experiment was performed, up to 10% conversion, in a cold room at 4°. From the ^{1}H-NMR-spectrum of the reaction mixture III_e could be observed.



IIIe



IIIf

In view of the 1/9 ratio observed for products III_a and III_b, and in view of the low conversion it is not possible to observe III_f in this experimental set-up. The NMR-data (100 MHz-spectrum, $CDCl_3$/TMS) of protons H_1, H_2 and H_3 and of the arylprotons of III_e are fully comparable with those of I_a:

aryl H : $\delta = 6.65$ ppm (m)

H_3: $\delta = 6.05$ ppm ($J_{2,3} = 8$ Hz)

H_2: $\delta = 6.35$ ppm (m) H_1: $\delta = 3.80$ ppm (m).

DISCUSSION

The "cubane-like" cyclomers can theoretically be formed by four different path ways (Scheme 5).

Way 2 in which the "cubane-like" cyclomer is directly formed by a 2(2Πs + 2Πs)-cyclomerization can be eliminated in view of the results of the irradiations during shorter times, in which only *endo*- or *endo*-Cope-rearranged cyclomers are formed.

Way 3 in which the "cubane-like" cyclomer results from a (2Πs + 2Πs)-cycloaddition of the *endo*-cyclomer can be excluded on the basis of the UV-spectrum of I_a (Fig. 4) together with the experimental conditions under which the cyclomerizations were performed.

The UV-spectrum of this compound is very similar to that of the intra-molecular photodimer of anthracene.[10] The slight hypochromism and bathochromic shift as compared to that of 2,3-dihydronaphthalene[11] can be attributed to interactions between the two chromophores.[12] As the irradiations were carried out in

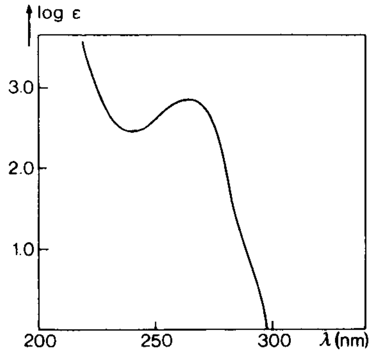
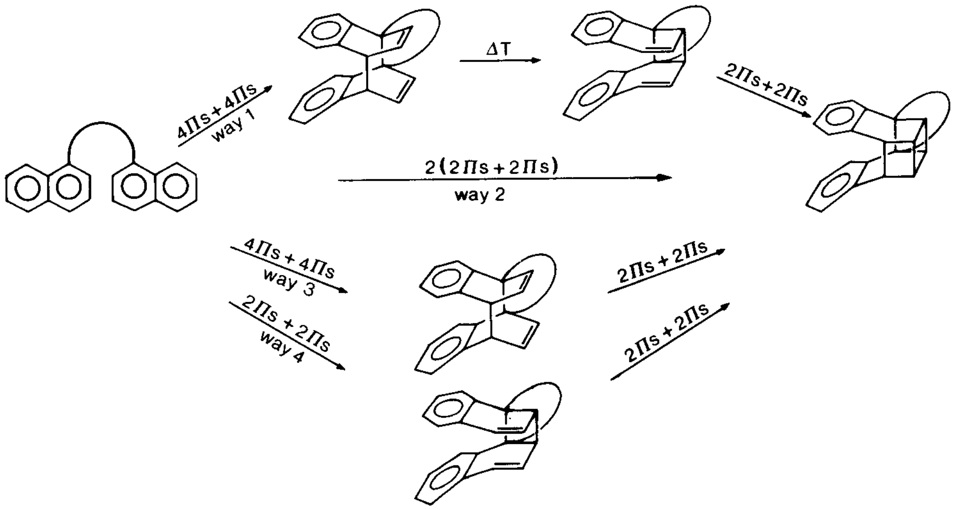


Fig. 4. U.V.-spectrum of I_a in iso-octane.



Scheme 5.

pyrex vessels and as *endo*-cyclomers don't absorb at wavelengths longer than 295 nm, it is obvious that the cubane-like cyclomers can not be formed directly from these *endo*-cyclomers. Even when the irradiations were performed with a filter solution, which absorbs all light below 300 nm, formation of cage-like cyclomers occurs, proving that way 3 is quite unlikely.

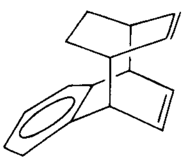
Way 4, in which the *endo*-Cope-rearranged cyclomer is directly formed by a ($2\Pi s + 2\Pi s$)-cyclomerization from the di-α-naphthyl compound, can be rejected on the basis of the following facts:

(a) Irradiation of I and III during shorter times and working up in the cold, resulted first in *endo*-cyclomer.

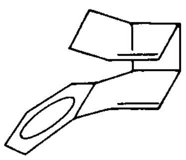
(b) Irradiation of 1,3-di-(α-naphthyl)propane by Chandross *et al.* yielded first *endo*-cyclomer, which upon standing Cope-rearranged.

(c) In the experiment of Yang *et al.*, in which the intermolecular cycloaddition of 1,3-cyclohexadiene to naphthalene was studied, irradiation resulted in the formation of *endo*-IVa, which upon heating was converted into IVb.

It can be concluded that way 1 constitutes the most plausible reaction scheme for the formation of cubane-like cyclomers from di-(α-naphthyl) compounds.



IVa



IVb

EXPERIMENTAL

UV-spectra were recorded on a Varian Spectrophotometer. ^1H-NMR spectra of the cyclomers were recorded on a Brucker 360 MHz instrument and on a Varian XL 100 instrument.

Photocyclomerization. The photocycloadditions were performed by irradiation of degassed solns ($\leq 10^{-3}$ M) of I, II and III in iso-octane, at room temp. in a Rayonet RS preparative photochemical reactor, equipped with 8 RUL-3000 Å lamps. After irradiation the solns were evaporated under reduced pressure and chromatographed as summarized in Table 4.

Di-(α-naphthylmethyl)ether I. To a soln of 2.4 g (100 mmol) NaH in 100 ml dry THF, 15.8 g (100 mmol) (α-naphthyl)methanol were added and stirred during 5 hr at room temp. 14.0 g (79 mmol) of α-(chloromethyl)-naphthalene were added slowly and the soln was stirred during an additional 24 hr. The mixture was poured into 500 ml H_2O and extracted with benzene. A first purification

Table 4. Irradiation time, chemical yield and chromatographic conditions.

Iso-octane solutions of compound	Irradiation time	Formed cyclomers	Chemical yield (%)[c]	Chromatographic conditions
I	5 hours	I_a, I_b and I_c[a]	98	Column chromatograhy on silica with benzene
	3 weeks	I_b and I_d ratio (1/3)	90	Thin-Layer chromatography on silica with THF
I_c	2 weeks	I_d	98	Thin-Layer chromatography on silica with THF
II	2 weeks	II_a and II_b ratio (1/5)	23	Thin-Layer chromatography on silica with n.pentane/CH_2Cl_2 (20/80)
III	3 hours[b]	III_a and III_b ratio (1/9)	10	HPLC on silica (10 µ) with n.hexane/diethylether (80/20)
	3 days	III_c and III_d ratio (1/9)	99	HPLC on silica (10 µ) with n.pentane/CH_2Cl_2/CH_3CN (75/15/10)

(a) Cyclomer I_c is obtained by refluxing a CH_2Cl_2-solution of I_a during two hours or by letting stand this solution during two days at room temperature.

(b) Working up of the reaction mixture occured at room temperature.

(c) The rest is recovered starting material; no other products were isolated.

was performed by column chromatography on silicagel with benzene. Preparative HPLC on silicagel ($10\,\mu$) with cyclohexane/CH_2Cl_2 (35/65), followed by recrystallization from benzene/n-pentane (90/10), yielded 8.9 g (38%) of colorless hexaëdric crystals with m.p. 120.5-121°. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.2 – 8.3 (m, 14 H), 5.10 (s, 4 H). IR: ν_{max}^{KBr}(cm^{-1}) 3040 w (=C–H); 1595 w, 1450 w (ring C–C); 1070 s, 1060 s (C–O–C); 785 s, 765 (C–H out of plane deformation) (Found: C, 88.72; H, 6.79; Calc. for $C_{22}H_{18}O$: C, 88.60; H, 6.10%).

[2-(α-*Naphthylethyl*)] (α-*naphthylmethyl*)*ether* II. Synthesis of this compound is analoguous to that of di-(α-naphthylmethyl)ether, starting from 2.4 g (100 mmol) NaH, 17.2 g (100 mmol) 2-(α-naphthyl)ethanol and 14.0 g (79 mmol) α-(chloromethyl)naphthalene. A first purification was performed by column chromatography on silicagel with benzene. Further purification was obtained by preparative HPLC on SiO_2($10\,\mu$) with cyclohexane/CH_2Cl_2 (50/50) followed by recrystallization from MeCN, which resulted in 8.6 g (35%) of white needles, m.p. 42.0–42.5°. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.2–8.3 (m, 14 H); 4.95 (s, 2 H); 3.35 (t, 2 H); 3.25 (t, 2 H). IR ν_{max}^{KBr} (cm^{-1}): 3040 w (=C–H); 1595 w, 1505 w, 1450 w (ring C–C); 1100 s, 1080 s, 1065 w (C–O–C); 785 s, 760 s (C–H out of plane deformation). (Found: C, 88.32; H, 6.72; Calcd for $C_{23}H_{20}O$: C, 88.40; H, 6.50%).

1,3-*Di*-(α-*naphthyl*)*propanol* III. To a soln of 0.7 g (18 mmol) $LiAlH_4$ in dry ether under N_2, slowly an ether soln of 3.1 g (10 mmol) of 1-α-naphthoyl-2-α-naphthylethylene[14] was added, so that a gently refluxing of the ether occurred. After all the α,α-chalcone was added, the excess of $LiAlH_4$ was destroyed by adding EtOAc, after which the mixture was filtrated. The filtrate was extracted with CH_2Cl_2, while the remaining ppt was dissolved in 2N H_2SO_4 and extracted with CH_2Cl_2. The CH_2Cl_2-portions were put together, and after evaporation of the CH_2Cl_2, the resulting pale yellow solid, was chromatographed on silicagel with benzene. Preparative HPLC on silica ($10\,\mu$) with n-hexane/CH_2Cl_2/MeCN (75/15/10), followed by recrystallization from cyclohexane afforded 2.4 g (78%) of colorless needles with m.p. 100.5–101°. ^{1}H-NMR ($CDCl_3$/TMS) δ (ppm): 7.3–8.2 (m, 14 H); 5.55 (t, 1 H); 3.34 (t, 2 H); 2.3 (m, 2 H); 2.00 (s, 1 H). IR ν_{max}^{KBr} (cm^{-1}): 3400–3200 m (O–H); 3030 m (=C–H); 2960 m (C–H); 1595(s), 1505(s), 1455(w) (ring C–C); 780(s); 760(s) (C–H out of plane deformation). (Found: C, 88.57; H, 6.55; Calcd for $C_{23}H_{20}O$: C–88.40; H, 6.50%).

Photocyclomers. All of the reported photocylomers show a molecular ion peak at a *m*/*e* which is identical to the *m*/*e* of the di-(α-naphthyl) compound from which they were formed.

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