Competition between Inter- and Intramolecular Photocycloaddition Reactions of 9-Substituted Anthracenes

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Received 21 March 2007; revised 27 April 2007

Abstract: A number of 9-[(arylmethoxy)methyl]anthracenes were prepared and their photoreactivity was studied. The intramolecular [4π+4π]cycloaddition competes with the intermolecular head-to-tail [4π+4π] cyclodimerization. The aryl substituents control the selectivity; concentration only plays a role in selectivity in certain cases. The complete reversibility of the cycloaddition makes this process suitable as a molecular switch, provided that traces of acids are avoided; when acid is present the cyclomers pursue an irreversible enol ether cleavage route.

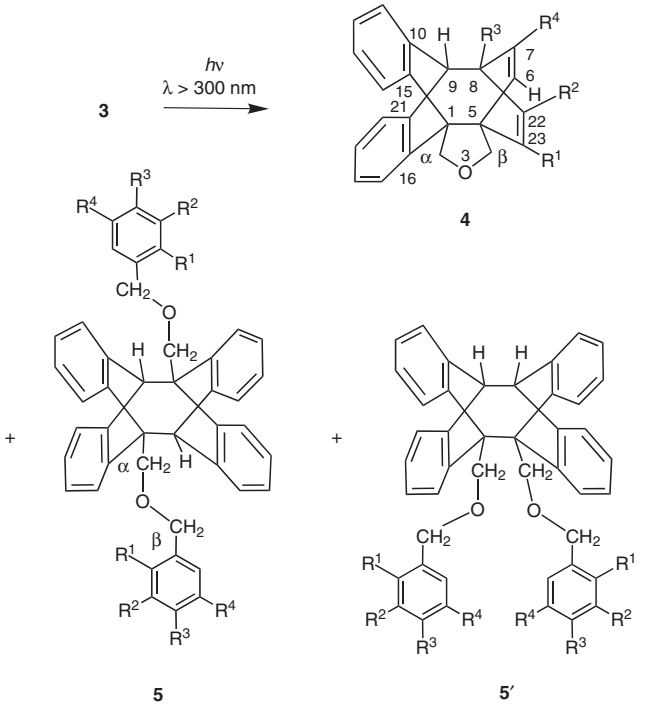
Key words: cycloaddition, cyclodimerization, ether cleavage, regioselectivity, retrocycloaddition

Reversible photochemical reactions between compounds that have different absorption (and/or emission) are of great interest for optical switching and optical data storage processes.[1] Recently, we developed such a system, which is based on the intramolecular [4π+4π] cycloaddition of benzene and anthracene moieties.[2] A prerequisite condition for this reaction is that the two chromophores are linked by a three-atom chain, like CH_2–O–CH_2. Useful switching systems should have clean, uniform reactions in both directions. The [4π+4π] cyclodimerization is an alternative photoreaction of anthracenes and is an old and well-known process.[1e,3] Therefore, we have now studied the competition between the desired intramolecular [4π+4π] cycloaddition and possible intermolecular [4π+4π] cyclodimerizations. For this purpose, 9-[(arylmethoxy)methyl]anthracenes **3** were generated. Their preparation was based on the nucleophilic substitution of **1** and **2** (Williamson synthesis), whereby the role of nucleophile and electrophile can be exchanged (Table 1, Methods A and B). The best results were obtained by using phase-transfer conditions (KOH, TBAB).

The possible photoproducts of **3a**–**n** are shown in Scheme 1.[4–8] Apart from the cyclomers **4**, head-to-tail dimers **5** and head-to-head dimers **5′** can be expected.[9,10] Compared to **5**, the dimers **5′** are highly thermolabile. In the past such compounds were usually detected in solution by NMR measurements of the crude product mixture. Nevertheless, many head-to-head dimers **5′** have been reported.[4,11,12]

In the first approximation, the compounds **3a**–**n** contain two separate chromophores. Therefore, selective irradiation (λ ≥300 nm) into the anthracene chromophore is possible. This precondition is necessary in order to prevent the light-induced reverse reactions **4**,**5**,**5′** → **3**. Table 2 shows the product ratios **4/5** that were obtained in the irradiation experiments of **3a**–**h**. The halogen-containing compounds **3i**–**k** are highly light sensitive. However, their irradiation yields product mixtures in which dimers, but no cyclomers, can be detected by ^{1}H NMR and FD-MS measurements; **3k** reacts even in daylight. Compound **3l** was studied in another context.[7] For the compounds **3a** and **3m**, no cyclomers **4a** and **4m** were reported, but mixtures of dimers **5a**/**5′a** and **5m**/**5′m**, respectively, were found;[4] on irradiation compound **3n** shows a quantitative intramolecular cycloaddition to give **4n**.[8]

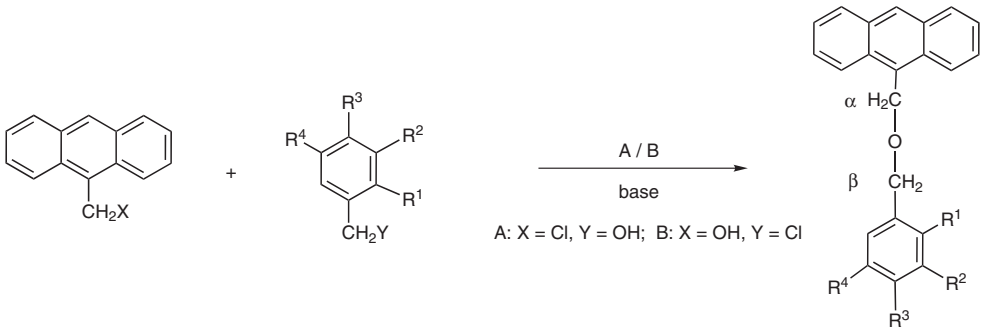
When a monomolecular reaction such as **3** → **4** competes with a bimolecular process, such as **3** + **3** → **5**, it would be expected that the concentration of the starting compound would determine the product ratio.



Scheme 1 Possible photoproducts of 9-substituted anthracenes **3**

SYNTHESIS 2007, No. 13, pp 1995–2001
Advanced online publication: 18.06.2007
DOI: 10.1055/s-2007-983734; Art ID: T05807SS

Table 1 Preparation of 9-[(Arylmethoxy)methyl]anthracenes **3a–n**



1 2a–n 3a–n

Product	R^1	R^2	R^3	R^4	A/B	Yield (%)	Ref.
3a	H	H	H	H	A	73	this work
					B	<50	4
3b	H	OMe	H	H	A	80	5
3c	H	H	OMe	H	A	79	this work
3d	H	OMe	H	OMe	A	82	6
3e	OMe	H	H	OMe	A	71	this work
3f	OMe	OMe	H	H	A	77	5
3g	H	OMe	OMe	OMe	A	63	6
3h	H	Me	H	Me	A	79	this work
3i	H	F	H	F	A	43	this work
3j	H	Cl	H	Cl	A	39	this work
3k	H	Br	H	H	A	28	this work
3l	H	H	NMe_2	H	B	–	7
3m	H	H	$(CH=CH)_2$		A	<50	4
3n	$(CH=CH)_2$		H	H	A	74	8

Table 2 Product Ratios on Irradiation of **3a–j**

Starting compound	Product ratio[a] **4/5**
3a	0:100
3b	44:56
3c	0:100
3d	100:0
3e	91:9
3f	0:100
3g	100:0
3h	0:100
3i	0:100
3j	0:100

[a] 1.8×10^{-3} M soln of **3a–h** in benzene; irradiation ($\lambda \geq 300$ nm).

However, Table 2 demonstrates that the majority of reactions are highly selective in one direction. The concentration has a notable effect in the cases **3b** → **4b**,**5b** and **3e** → **4e**,**5e**. At a concentration of 1.8 mM the ratio **4b/5b** is 44:56, at ca. 3.0 mM only small amounts of **4b** are formed and **5b** is obtained in 82% isolated yield.[5] The preferred reaction route can even be altered in the case of **3e**. The ratio 91:9 of **4/5** shown in Table 2 can be changed to 22:78 when the concentration of **3e** is raised from 1.8 mM to 113.0 mM. Dilution does not favor the generation of cyclomers in cases where dimers (and oligomers) are the sole products, as apparent in the ^{1}H NMR reaction spectra of **5a**,**c**,**f**,**h–j**. Due to the aggregation of the anthracenes, dimerization works also in these cases in 0.1 mM solutions.

The structure determination of the dimers **5a–c**,**e**,**f**,**h–j** was much more complicated. We recently described the crystal structure of compound **3f** and its structure in solution, which is characterized by different rotamers.[5] Tem-

perature-dependent ^1H and ^{13}C NMR spectra reveal the same phenomenon for all head-to-tail dimers studied here. The number of resonance signals at room temperature is much higher than that would be expected for a single structure **5**.

Figure 1 shows the 2D NMR spectrum HMQC of **5c** in the high field region. The signals ($CDCl_3$, 5 °C) reveal the presence of three rotamers. Figure 2 shows the staggered conformers **A**, **B**, and **C**. The OR group can have an antiperiplanar orientation related to the C–C bond that was generated in the dimerization. Steric hindrance of OR and the hydrogen atoms at the condensed benzene rings results then in a 'frozen' rotation at this temperature. Thus rotamer **A** has a relatively rigid C_{2h} structure. When both OR groups have skew orientations to the newly formed C–C bonds, as realized in **C**, partial rotation provokes a fast equilibration between the drawn structure **C**(C_2), its enantiomer, and the structure **C**(C_i), which is obtained from **C**(C_2) by a 120° rotation on one side. Thus, C_{2h} symmetry is valid for this conformer also. Finally in rotamer **B**, an antiperiplanar OR orientation is given on one side and a flexible skew orientation on the other; the result is de facto C_s symmetry. Accordingly **B** has twice as many ^1H and ^{13}C NMR signals as **A** and **C**. Therefore, the assignment of the NMR signals of **B** in Figure 1 is apparent. The differentiation between **A** and **C** is much more difficult. The benzene rings of the side chains in **C** can lie above the bridgehead protons, so that the high-field singlet at δ = 3.54 can be assigned to the bridgehead protons of **C**; proof for this assignment was found by NOE measurements. The antiperiplanar arrangement of the OR groups in **A** leads to the neighborhood of the bridgehead proton and the two α-CH_2 protons, whereas in rotamer **C** only one α-CH_2 proton is close to the bridgehead. Thus the different signal enhancement in the NOE difference spectra indicates the assignments given for **5c** in Figure 1. The NMR data of the dimers **5a**,**b**,**e**,**f**,**h** are very similar, so that analogous rotamers can be assumed as for **5c**. To our best knowledge, there is only one rotamer discussion in the literature of anthracene dimers, namely for 1-hydroxy-1-methylethyl side chains.[13] However, antiperiplanar arrangements of the OH groups, comparable to the arrangement of the OR groups on one side of **B** and both sides of **A**, were not found.

When the NMR measurement of **5c** in 1,1,2,2-tetrachloroethane-d_2 is performed at 90 °C, the signals collapse as demonstrated in Figure 1. At this temperature the rotation of both side chains is fast in terms of the NMR timescale, so that in ^1H and ^{13}C NMR spectroscopy one signal appears for the bridgehead CH, α-CH_2, β-CH_2, and OCH_3

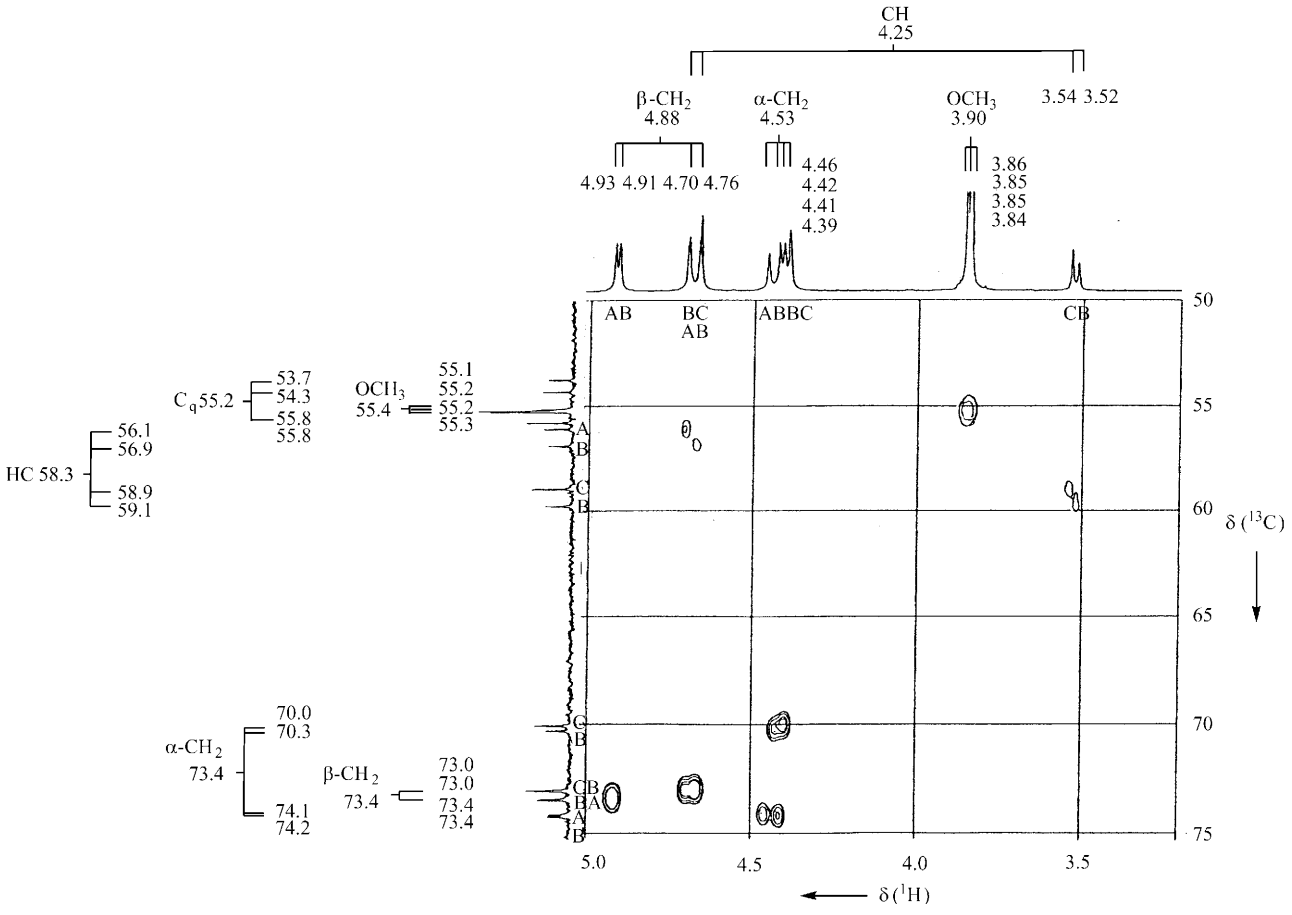


Figure 1 High-field region of the 2D NMR (HMQC) spectrum of **5c** (400 MHz, $CDCl_3$, 5 °C); The ^1H and ^{13}C NMR signals correspond to the three rotamers **A**, **B**, and **C** shown in Figure 2. Heating ($CDCl_2CDCl_2$, 90 °C) leads to the collapse of the singlets demonstrated for OCH_3, α-CH_2, β-CH_2, CH and C_q (The signals for C_q and OCH_3 could not be definitely assigned to the rotamers **A**, **B**, and **C**.).

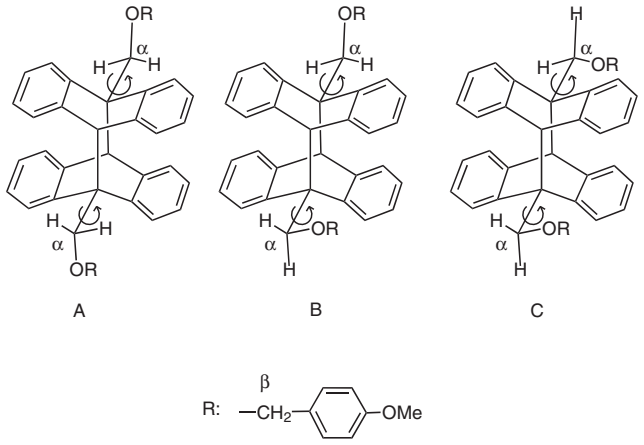
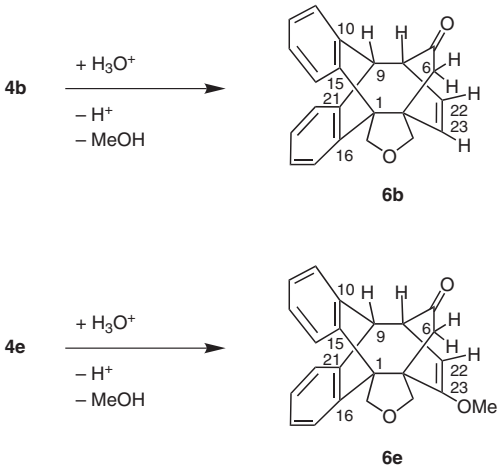


Figure 2 Rotamers of **5a** that exist in solution (CH_2Cl_2, $CHCl_3$, $CHCl_2CHCl_2$, benzene)

groups each; α- and β-CH_2 groups are then coincidentally isochronous.

The other dimers **5a**,**b**,**e**,**f**,**h** exhibit analogous restriction of the rotation of the side chains. Head-to-head dimers were not found. The photodimerization of **3i** and **3j** is too non-uniform to permit a final statement.

In contrast to the reversibility **4** → **3**, the cleavage of the dimers **5** → **3** is sufficiently clean. Therefore, we focused our studies on the switching process **3** → **4**. A complete thermal or photochemical back reaction **4** → **3** is feasible in the absence of acids; even traces of acids, present, for example, chloroform that has not been recently purified, disturb and transform the cyclomers to ketones. Scheme 2 shows the generation of the monoketones **6b** and **6e** from **4b** and **4e**, respectively. The other cyclomers **4d** and **4g** have comparable sensitivity toward acids, but additionally the enol ether cleavage can be accompanied by a scaffold rearrangement.[6] All resulting ketones are incapable of photochemical or thermal cleavage to 9-[(aryl-methoxy)methyl]anthracenes in which the aryl group would be a phenol unit.



Scheme 2 Enol ether cleavage of **4b**,**e** to the monoketones **6b**,**e**

Summarizing the applicability of the systems discussed herein, we can make the statement that the intramolecular cycloadditions/cycloreversions **3d** ⇆ **4d** and **3g** ⇆ **4g** are best suited as molecular switches. These monomolecular processes are so effective that the bimolecular anthracene–anthracene dimerization has no chance, not even in concentrated solutions. The common feature of **3d** and **3g** is high electron density at the 4-position of the benzene ring. Although [4π+4π] cycloaddition may be allowed as a concerted photoreaction, a stepwise process, in which the first excited singlet state S_1 located in the anthracene moiety undergoes an electron transfer from the electron-rich benzene ring, seems to be plausible. Absorption and fluorescence, which are typical for the anthracene chromophore, disappear in the quantitative step **3d**,**g** → **4d**,**g** and are recovered completely in the reverse process **4d**,**g** → **3d**,**g**. The optical switching is based on the separation of the chromophores; **3d**,**g** show the anthracene absorption with its typical vibrational structure between 325 and 410 nm and the absorption of the benzenoid ππ* transitions below 300 nm. The cyclomers **4d**,**g** have only superimposed benzene and homodiene absorptions below 290 nm. Between 290/300 and 325 nm is an absorption gap.

Melting points were measured with a Büchi melting point apparatus and are uncorrected. FT-IR spectra were obtained with a Perkin-Elmer GX/200 and UV/Vis spectra with a Zeiss MCS 320/340 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with the Bruker spectrometer AMX 400. $CDCl_3$ served as solvent, unless otherwise noted, and TMS was used as the internal standard. The symbol 's' is used, when a ^2J or ^3J coupling is not visible in a routine ^{1}H NMR spectrum. Field desorption (FD) MS were obtained with a Finnigan MAT 95 and ESI (electrospray ionization) MS with a Micromass QTOF Ultima-3 spectrometer. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Mainz.

9-[(Benzyloxy)methyl]anthracenes 3a–k; General Procedure

To 9-(chloromethyl)anthracene[14] (**1**, X = Cl, 1.13 g, 5.0 mmol), benzyl alcohol **2a**–**k**[14] (5.5 mmol), and TBAB (0.34 g, 1.05 mmol) in chlorobenzene (20 mL), a soln of KOH (0.8 g, 14.3 mmol) in H_2O (1 mL) was added. The mixture was stirred at 60 °C under argon for 3 d. H_2O (70 mL) was added and the soln extracted with CH_2Cl_2 (70 mL) and then the aqueous layer was extracted with $CHCl_3$ (100 mL). The combined organic phases were dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography (3 × 40 cm, silica gel, cyclohexane–CH_2Cl_2–EtOAc, 1:1:0.03).

Compounds **3b**,[5] **3d**,[6] **3f**,[5] and **3g**[6] have been previously described.

9-[(Benzyloxy)methyl]anthracene (3a)

Yellowish solid; yield: 1.085 g (73%); mp 60 °C.

^{1}H NMR ($CDCl_3$): δ = 4.27 (s, 2 H, β-CH_2), 5.49 (s, 2 H, α-CH_2), 7.31–7.54 (m, 9 H, H_{arom}), 8.00–8.02 (m, 2 H, H_{arom}), 8.30–8.32 (m, 2 H, H_{arom}), 8.46 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 64.1 (α-CH_2), 72.4 (β-CH_2), 124.4, 124.9, 126.1, 128.0, 128.0, 128.4, 129.0, 129.0 (CH_{arom}), 128.0, 131.1, 131.4, 138.4 (C_q arom).

MS (FD): *m*/*z* (%) = 298 (100) [M$^+$].

Anal. Calcd for $C_{22}H_{18}O$ (298.4): C, 88.56; H, 6.08. Found: C, 88.65; H, 6.11.

9-[(4-Methoxybenzyloxy)methyl]anthracene (3c)
Yellowish solid; yield: 1.290 g (79%); mp 78 °C.

^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 4.68 (s, 2 H, β-CH_2), 5.46 (s, 2 H, α-CH_2), 6.95, 7.37 (AA′BB′, 4 H, H_{phenyl}), 7.41–7.58 (m, 4 H, $H_{anthracene}$), 8.00–8.03 (m, 2 H, $H_{anthracene}$), 8.29–8.32 (m, 2 H, $H_{anthracene}$), 8.46 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH_3), 63.7 (α-CH_2), 72.0 (β-CH_2), 113.7, 124.3, 124.8, 126.0, 128.3, 128.9, 129.6 (CH_{arom}), 128.7, 130.4, 131.0, 131.4 (C_q arom).

MS (FD): *m*/*z* (%) = 328 (100) [M$^+$].

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{20}NaO_2$: 351.1361; found: 351.1381.

9-[(2,5-Dimethoxybenzyloxy)methyl]anthracene (3e)
Yellowish solid; yield: 1.270 g (71%); mp 124 °C.

^{1}H NMR ($CDCl_3$): δ = 3.69 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.76 (s, 2 H, β-CH_2), 5.52 (s, 2 H, α-CH_2), 6.80 ('s', 2 H, H_{phenyl}), 7.00 ('s', 1 H, H_{phenyl}), 7.41–7.52 (m, 4 H, $H_{anthracene}$), 7.98–8.00 (m, 2 H, $H_{anthracene}$), 8.34–8.36 (m, 2 H, $H_{anthracene}$), 8.44 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 55.7, 56.0 (OCH_3), 64.5 (α-CH_2), 67.2 (β-CH_2), 111.5, 113.7, 114.9, 124.5, 124.9, 126.1, 128.3, 128.9 (CH_{arom}), 127.8, 131.1, 131.5, 131.5 (C_q arom), 151.5, 153.7 (OC_q arom).

MS (EI): *m*/*z* (%) = 358 (50) [M$^+$], 192 (100), 179 (72), 151 (50).

Anal. Calcd for $C_{24}H_{22}O_3$ (358.4): C, 80.42; H, 6.19. Found: C, 80.43; H, 6.23.

9-[(3,5-Dimethylbenzyloxy)methyl]anthracene (3h)
Yellowish solid; yield: 1.290 mg (79%); mp 90 °C.

^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6 H, CH_3), 4.65 (s, 2 H, β-CH_2), 5.46 (s, 2 H, α-CH_2), 6.95 ('s', 1 H, H_{phenyl}), 7.02 ('s', 2 H, H_{phenyl}), 7.43–7.53 (m, 4 H, $H_{anthracene}$), 7.99–8.02 (m, 2 H, $H_{anthracene}$), 8.30–8.32 (m, 2 H, $H_{anthracene}$), 8.45 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_3), 64.0 (α-CH_2), 72.5 (β-CH_2), 124.5, 124.9, 125.9, 126.1, 128.4, 129.0, 129.3 (CH_{arom}), 128.5, 131.1, 131.5, 138.2, 138.2 (C_q arom).

MS (FD): *m*/*z* (%) = 327 (100) [M + H$^+$].

Anal. Calcd for $C_{24}H_{22}O$ (326.4): C, 88.31; H, 6.79. Found: C, 88.27; H, 6.80.

9-[(3,5-Difluorobenzyloxy)methyl]anthracene (3i)
Yellowish solid; yield: 720 mg (43%); mp 139 °C.

^{1}H NMR ($CDCl_3$): δ = 4.62 (s, 2 H, β-CH_2), 5.53 (s, 2 H, α-CH_2), 6.67–6.75 (m, 1 H, H_{phenyl}), 6.86–6.90 (m, 2 H, H_{phenyl}), 7.45–7.57 (m, 4 H, $H_{anthracene}$), 8.00–8.03 (m, 2 H, $H_{anthracene}$), 8.30–8.32 (m, 2 H, $H_{anthracene}$), 8.47 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 64.5 (α-CH_2), 70.9 (β-CH_2), 102.9 (t, ^2J(C,F) = 25 Hz, CH_{phenyl}), 110.1 (CH_{phenyl}), 124.1, 125.0, 126.4, 128.7, 129.1 (C_q anthracene), 142.6 (C_i phenyl), 163.0 (dd, ^1J(C,F) = –247 Hz, ^3J(C,F) = 16 Hz, *C*F).

MS (FD): *m*/*z* (%) = 334 (100) [M$^+$].

Anal. Calcd for $C_{22}H_{16}F_2O$ (334.4): C, 79.03; H, 4.82. Found: C, 79.03; H, 4.82.

9-[(3,5-Dichlorobenzyloxy)methyl]anthracene (3j)
Yellowish solid; yield: 720 mg (39%); mp 97 °C.

^{1}H NMR ($CDCl_3$): δ = 4.58 (s, 2 H, β-CH_2), 5.51 (s, 2 H, α-CH_2), 7.21 (d, ^4J = 1.8 Hz, 2 H, H_{phenyl}), 7.26 (d, ^4J = 1.8 Hz, 1 H, H_{phenyl}), 7.45–7.57 (m, 4 H, $H_{anthracene}$), 8.00–8.03 (m, 2 H, $H_{anthracene}$), 8.30–8.33 (m, 2 H, $H_{anthracene}$), 8.47 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 64.5 (α-CH_2), 70.6 (β-CH_2), 124.1, 125.0, 126.0, 126.4, 127.7, 128.7, 129.1 (CH_{arom}), 127.9, 131.1, 131.4, 134.9, 142.0 (C_q arom).

MS (EI): *m*/*z* (%) = 366 (29, Cl_2 isotope pattern) [M$^+$].

HRMS: m/z [M($^{35}Cl_2$)]$^+$ calcd for $C_{22}H_{16}{}^{35}Cl_2$: 366.0576; found: 366.0580.

9-[(3-Bromobenzyloxy)methyl]anthracene (3k)
Yellowish solid; yield: 530 mg (28%); mp 102 °C.

^{1}H NMR ($CDCl_3$): δ = 4.64 (s, 2 H, β-CH_2), 5.49 (s, 2 H, α-CH_2), 7.18–7.30 (m, 2 H, H_{phenyl}), 7.41–7.56 (m, 6 H, $H_{anthracene}$, H_{phenyl}), 8.00–8.02 (m, 2 H, $H_{anthracene}$), 8.28–8.31 (m, 2 H, $H_{anthracene}$), 8.46 (s, 1 H, H10).

^{13}C NMR ($CDCl_3$): δ = 64.2 (α-CH_2), 71.3 (β-CH_2), 124.2, 124.9, 126.2, 126.3, 128.5, 129.0, 129.9, 130.7, 130.8 (CH_{arom}), 122.5, 128.2, 131.0, 131.4, 140.8 (C_q arom).

MS (FD): *m*/*z* (%) = 376/378 (100, Br isotope pattern), [M$^+$].[15]

Irradiation of the Anthracene Derivatives 3a–h
An argon stream was purged for 30 min through a dilute soln of **3a–h** [0.30 mmol in anhyd benzene (165 mL)]. The soln was irradiated with a Hanovia-450 W medium-pressure Hg lamp, equipped with a Duran glass filter (λ ≥300 nm). During the irradiation period of 15–30 min, a slow argon stream was maintained. Evaporation of the solvent at 20 °C under reduced pressure gave the photoproducts as a solid residue; they were purified by crystallization (CH_2Cl_2–EtOH, 1:2). In the case of **3b** and **3e** mixtures **4b/5b** and **4e/5e** respectively were obtained, which could be separated by fractional crystallization (CH_2Cl_2–EtOH), because the dimers **5b** and **5e** have much lower solubility.

Compounds **4b**,[5] **5b**,[5] **4d**,[6] **5f**,[5] and **4g**[6] have been previously characterized.

5,11-Bis[(benzyloxy]methyl]-5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]dibenzenodibenzo[*a*,*e*]cyclooctene (5a)
Colorless crystals; yield: 43 mg (48%); mp 226 °C (dec.).

FT-IR (KBr): 1475, 1453, 1135, 1109, 1028, 777, 746, 733, 693 cm^{-1}.

^{1}H NMR ($CDCl_3$, 25 °C): δ = 3.53 (s)/4.70 (s) (2 H, bridgehead H), 4.47 (s)/4.49 (s) (4 H, α-CH_2), 4.75 (s)/4.99 (s) (4 H, β-CH_2), 6.75–7.64 (m, 26 H, H_{arom}).

MS (FD): *m*/*z* (%) = 597 (12) [M$^+$], 298 (100).

Anal. Calcd for $C_{44}H_{36}O_2$ (596.8): C, 88.56; H, 6.08. Found: C, 88.09; H, 6.15.

5,11-Bis[(4-methoxybenzyloxy)methyl]-5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]dibenzenodibenzo[*a*,*e*]cyclooctene (5c)
Colorless crystals; yield: 25 mg (25%); mp 198 °C (dec.).

FT-IR (KBr): 1512, 1247, 1171, 1095, 1030, 817, 758, 694 cm^{-1}.

^{1}H NMR ($CDCl_3$, 25 °C): δ = 3.52 (s)/4.68 (s,) (2 H, bridgehead H), 3.84 (s)/3.85 (s) (6 H, OCH_3), 4.42 (s)/4.44 (s) (4 H, α-CH_2), 4.68 (s)/4.92 (s) (4 H, β-CH_2), 6.75–7.56 (24 H, H_{arom}).

^{1}H NMR ($CDCl_3$, 0 °C): δ = 3.52 (s)/3.54 (s)/4.67 (s)/4.70 (s) (2 H, bridgehead H), 3.84 (s)/3.85 (s)/3.86 (s) (6 H, OCH_3), 4.39 (s)/4.41 (s)/4.42 (s)/4.46 (s) (4 H, α-CH_2), 4.67 (s)/4.70 (s)/4.91 (s)/4.93 (s) (4 H, β-CH_2), 6.76–7.56 (m, 24 H, H_{arom}).

^{1}H NMR ($CDCl_2CDCl_2$, 90 °C): δ = 3.90 (s, 6 H, OCH_3), 4.25 (br s, 2 H, bridgehead H), 4.53 (s, 4 H, α-CH_2), 4.88 (s, 4 H, β-CH_2), 6.78–6.85 (m, 4 H, H_{arom}), 6.87–6.89 (m, 8 H, H_{arom}), 7.03/7.51 (AA′BB′, 8 H, H_{phenyl}), 7.14 (m, 4 H, H_{arom}).

^{13}C NMR ($CDCl_3$, 0 °C): δ = 53.7, 54.3, 55.8 (C_q, bridgehead), 55.1, 55.2, 55.2, 55.3 (OCH_3), 56.1, 56.9, 58.9, 59.7 (CH, bridgehead), 70.0, 70.3, 74.1, 74.2 (α-CH_2), 73.0, 73.0, 73.4, 73.4 (β-CH_2), 113.6, 113.8, 123.4, 123.9, 124.7, 125.1, 125.3, 125.4, 127.2, 127.7, 127.8, 129.3, 129.4, 129.5, 129.9 (CH_{arom}, partially superimposed), 128.1, 128.7, 142.5, 142.6, 142.7, 142.9, 143.3, 143.7, 144.8, 159.0, 159.1 (C_q arom, partially superimposed).

^{13}C NMR ($CDCl_2CDCl_2$, 90 °C): δ = 55.2 (C^q, bridgehead), 55.4 (OCH_3), 58.3 (CH, bridgehead), 73.4 (α-CH_2, β-CH_2), 114.2, 129.5 (CH_{phenyl}), 124.4, 125.1, 125.3, 127.7 (CH_{arom}), 130.3, 159.5 (C_q phenyl), 143.3, 144.2 (C_q arom).

MS (FD): *m*/*z* = 657 (5) [M + H$^+$], 328 (100).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{46}H_{40}NaO_4$: 679.2824; found: 679.2806.

7,23-Dimethoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-6,10,12,14,16,18,20,22-octaene (4e)

Yellowish solid; yield: 91 mg (85%); mp 122 °C (dec.).

FT-IR (KBr): 1716, 1634, 1499, 1471, 1231, 1219, 1157, 1135, 1068, 1020, 756 cm^{-1}.

^{1}H NMR (C_6D_6/TMS): δ = 2.69 (s, 3 H, OCH_3), 2.73 (s, 3 H, OCH_3), 3.61/4.73 (AB, ^2J = –9.0 Hz, 2 H, H4), 3.14 (ddd, ^3J = 10.7 Hz, ^3J = 7.7 Hz, ^4J = 2.3 Hz, 1 H, H8), 4.04 (d, ^3J = 10.7 Hz, 1 H, H9), 4.06 (d, ^4J = 2.3 Hz, 1 H, H_{olefin}), 4.21 (d, ^3J = 7.7 Hz, 1 H, H_{olefin}), 4.55 ('s', 2 H, H2), 6.75–7.28 (m, 8 H, H_{arom}).

^{13}C NMR (C_6D_6/TMS): δ = 44.1 (C8), 54.2 (C9), 54.9 (O*C*H$_3$), 54.9 (O*C*H$_3$), 66.0 (C1), 61.1 (C5), 71.3 (C2), 75.2 (C4), 99.0 (CH_{olefin}), 103.4 (CH_{olefin}), 123.6, 123.6, 125.1, 125.3, 125.8, 125.9, 127.0 127.3 (CH_{arom}), 145.6, 145.9, 145.9, 146.4 (C_q), 165.5 (OC_q), 167.1 (OC_q).

MS (FD): *m*/*z* = 358 (100) [M$^+$].

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{22}NaO_3$: 381.1467; found: 381.1462.

5,11-Bis[(2,5-dimethoxybenzyloxy)methyl]-5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]dibenzenodibenzo[*a*,*e*]cyclooctene (5e)

Yield: 9 mg (8%); mp 225 °C (dec.). When the concentration of **3e** (72 mg) in benzene was enhanced to 5.4 mM, the yield of **5e** increased to 16 mg (22%) and the yield of **4e** decreased to 50 mg (69%). At 113 mM (40.5 mg **3e** in 1.0 mL benzene), the ratio **4**:**5** amounts to 22:78.

FT-IR (KBr): 1501, 1474, 1455, 1279, 1246, 1218, 1160, 1105, 1053, 1034, 694 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.54 (s)/4.74 (s) (2 H, bridgehead), 3.67 (s)/3.80 (s) (6 H, OCH_3), 3.88 (s, 6 H, OCH_3), 4.53 (s)/4.56 (s) (4 H, α-CH_2), 4.78 (s)/4.99 (s) (4 H, β-CH_2), 6.71–7.31 (m, 22 H, H_{arom}).

MS (FD): *m*/*z* = 717 (4) [M + H$^+$], 359 (100).

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{48}H_{44}NaO_6$: 739.3036; found: 739.3046.

5,11-Bis[(3,5-dimethylbenzyloxy)methyl]-5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1″,2″]dibenzenodibenzo[*a*,*e*]cyclooctene (5h)

Colorless solid; yield: 25 mg (26%); mp 208 °C (dec.).

FT-IR (KBr): 1677, 1474, 1455, 1352, 1285, 1136, 1111, 778, 694 cm^{-1}.

^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.34 (s)/2.39 (s) (12 H, CH_3), 3.54 (s)/4.77 (s) (2 H, bridgehead), 4.45 (s)/4.49 (s) (4 H, α-CH_2), 4.68 (s)/4.93 (s) (4 H, β-CH_2), 6.76–7.26 (m, 22 H, H_{arom}).

^{1}H NMR ($CDCl_3$, –20 °C): δ = 2.35 (s)/2.36 (s)/2.40 (s) (12 H, CH_3), 3.56 (s)/3.57 (s)/4.78 (s)/4.80 (s) (2 H, bridgehead), 4.42 (s)/4.44 (s)/4.46 (s)/4.49 (s) (4 H, α-CH_2), 4.67 (s)/4.71 (s)/4.93 (s)/4.95 (s) (4 H, β-CH_2), 6.77–7.27 (m, 22 H, H_{arom}).

MS (FD): *m*/*z* = 653 (6) [M + H$^+$].

Anal. Calcd for $C_{48}H_{44}O_2$ (652.9): C, 88.31; H, 6.79. Found; C, 88.31; H, 6.81.

Irradiation of the Anthracene Derivatives 3i,j

An argon purged soln of **3i** (14.0 mg, 0.042 mmol) or **3j** (21.4 mg, 0.058 mmol) in benzene-d_6 (1 mL) was irradiated with a Hanovia 450W middle-pressure lamp equipped with a Duran glass filter. Reaction spectra after 5, 15, and 35 min revealed the generation of the dimers **5i** or **5j** and the absence of the cyclomers **4i** or **4j**. Both photoreactions are non-uniform and the enrichment of the dimers did not exceed 20%. Therefore we did not isolate and purify **5i** or **5j**. (Compound **3k** decomposed already in daylight.)

Enol Ether Cleavage

The photoproducts **4** can be subjected to an enol ether cleavage according to the literature.[6] However, the monoketones **5b** and **6e** could also be obtained in a one-pot reaction from **3b** and **3e**, respectively. After the irradiation as described above, the solvent was removed and the residue was treated with toluene (30 mL) and HCO_2H (0.5 mL, 610 mg, 13.25 mmol) at 0 °C for 1 h. Column chromatography (30 × 2 cm, silica gel, cyclohexane–EtOAc, 97:3 to 92:8) yielded the crude monoketones **6b**,**e**, which could be recrystallized (CH_2Cl_2–cyclohexane, 1:9).

(5*R,8*R**)-3-Oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-10,12,14,16,18,20,22-heptaen-7-one (6b)**

From **4b** (132 mg); colorless solid; yield: 26 mg (21%); mp 177 °C.

^{1}H NMR (C_6D_6): δ = 1.84/1.99 (AB, ^2J = –18.7 Hz, 2 H, H6), 3.56 (m, 1 H, H8), 3.64/4.36 (AB, ^2J = –11.4 Hz, 2 H, H4), 4.02 (d, ^3J = 8.8 Hz, 1 H, H9), 4.66/4.85 (AB, ^2J = –10.3 Hz, 2 H, H2), 5.53–5.56 (m, 1 H, H22), 5.74 (d, ^3J = 8.8 Hz, 1 H, H23), 7.13–7.29 (m, 7 H, H_{arom}), 7.49–7.51 (m, 1 H, H_{arom}).

^{13}C NMR (C_6D_6): δ = 44.1 (C6), 50.5 (C9), 54.7 (C5), 56.5 (C8), 60.7 (C1), 72.3 (C2), 80.4 (C4), 123.7, 124.2, 126.5, 126.6, 127.2, 127.3, 127.5, 128.9 (CH_{arom}), 129.9, 142.1 (CH_{olefin}), 141.0, 141.1, 141.9, 144.4 (C_q arom), 211.1 (CO).

MS (FD): *m*/*z* = 315 (100) [M + H$^+$].

Anal. Calcd for $C_{22}H_{18}O_2$ (314.4): C, 84.05; H, 5.77. Found: C, 83.94; H, 5.71.

(5*R,8*R**)-23-Methoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]-tricosa-10,12,14,16,18,20,22-heptaen-7-one (6e)**

From **4e** (72 mg); colorless solid; yield: 36 mg (52%); mp 107 °C.

^{1}H NMR (C_6D_6): δ = 1.78/1.93 (AB, ^2J = –18.4 Hz, 2 H, H6), 2.56 (s, 3 H, OCH_3), 3.01/4.54 (AB, ^2J = –9.2 Hz, 2 H, H4), 3.41 (dd, ^3J = 11.4 Hz, ^3J = 7.7 Hz, 1 H, H8), 3.81 (d, ^3J = 7.7 Hz, 1 H, H22), 4.07 (d, ^3J = 11.4 Hz, 1 H, H9), 4.32/4.54 (AB, ^2J = –10.3 Hz, 2 H, H2), 6.75–6.78 (m, 1 H, H_{arom}), 6.90–7.03 (m, 6 H, H_{arom}), 7.46–7.49 (m, 1 H, H_{arom}).

^{13}C NMR (C_6D_6): δ = 44.6 (C6), 51.1 (C8), 54.1, 54.7 (C9, OCH_3), 56.9, 60.9 (C1, C5), 72.3, 74.4 (C2, C4), 94.9 (C22), 124.3, 125.0, 126.0, 126.5, 127.1, 127.3, 129.1 (CH_{arom}, partly superimposed), 140.9, 142.1, 143.2, 144.7 (C_q arom), 164.9 (C23), 207.8 (CO).

MS (FD): *m*/*z* = 344 (100) [M$^+$].

Anal. Calcd for $C_{23}H_{20}O_3$ (344.4): C, 80.21; H, 5.85. Found: C, 80.21; H, 5.85.

Cleavage of the Cyclomers 4 (Back Reaction)

In the absence of acid, heating of **4** (neat) to 110 °C provoked a fast and quantitative back reaction to **3**. Irradiation with λ = 254 nm had

the same result. The number of possible switching cycles is not known, but it should be high, because extended irradiation (48 h) did not show any aging effects.

Acknowledgment

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the National Natural Science Foundation of China (20272059, 20572111) and to Specialized Chinese Research Fund for the Doctoral Program of Higher Education (20060561024) for financial support. We thank Prof. Henri Bouas-Laurent (University of Bordeaux) for many valuable discussions on this topic.

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