Intramolecular [2 + 2] Photocycloaddition, 3[1] Synthesis of 1,2-Ethano[2.*n*]metacyclophanes from Styrene Derivatives

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Several 1,2-ethano[2.*n*]metacyclophanes were prepared from α,ω-bis(*m*-vinylphenyl)alkanes by the title reaction in reasonable yields. Reactions of 1,3-bis(*m*-vinylphenyl)propane and 1,4-bis(*m*-vinylphenyl)butane gave *cis*- and *trans*-cyclophanes in a ca. 4:1 ratio. The reaction was studied in several solvents with and without additives. Under direct irradiation, a weak solvent effect was observed, while addition of benzophenone and *p*-dicyanobenzene exerted a considerable effect. The mechanism is discussed in comparison with that of paracyclophane synthesis.

Intramolekulare [2 + 2]-Photocycloaddition, 3[1]. – Darstellung von 1,2-Ethano[2.*n*]metacyclophanen aus Styrol-Derivaten

Einige 1,2-Ethano[2.*n*]metacyclophane wurden aus α,ω-Bis(*m*-vinylphenyl)alkanen mit Hilfe der Titelreaktion in guten Ausbeuten hergestellt. Die Reaktion mit 1,3-Bis(*m*-vinylphenyl)propan und 1,4-Bis(*m*-vinylphenyl)butan lieferte *cis*- und *trans*-Cyclophane im Verhältnis von ca. 4:1. Die Reaktion wurde in verschiedenen Lösungsmitteln in Gegenwart und Abwesenheit weiterer Additionspartner studiert. Der schwache Lösungsmitteleinfluß bei direkter Bestrahlung und die deutliche Auswirkung von Benzophenon- und *p*-Dicyanobenzol-Zusätzen werden erklärt. Der Mechanismus wird im Vergleich mit dem der Paracyclophan-Bildung diskutiert.

Photocyclodimerization of styrene was discovered two decades ago and investigated extensively[2]. To date, there have been several mechanistic investigations of the reaction of styrene derivatives. Shirota and co-workers described the photocyclodimerization of β-vinylnaphthalene in detail[2i]. Addition of triethylamine or diazabicyclooctane was found to increase the *trans*/*cis* ratio of the cyclodimer produced. Charge-transfer interaction between the excited vinylnaphthalene and the ground state amine quenched the reaction via the vinylnaphthalene singlet state, which otherwise gives the *cis*-cyclodimer. Accordingly, the relative population of the vinylnaphthalene triplet state, which yields the *trans*-cyclodimer, is increased.

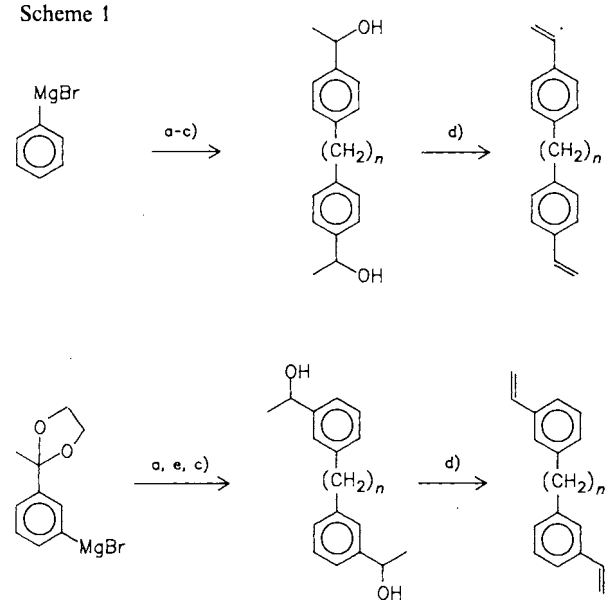
As reported briefly[1a], the intramolecular [2 + 2] photocycloaddition of several α,ω-bis(vinylaryl)alkanes gives cyclophanes in reasonable and sometimes excellent yields. We recently observed that the reaction of α,ω-bis(*m*-vinylphenyl)alkanes affords 1,2-ethano[2.*n*]metacyclophanes in yields of 31 to 80%, and in a few cases both *cis*- and *trans*-cyclobutane-ring-containing cyclophanes are formed. In this paper, we would like to report in detail on the intramolecular version of this styrene [2 + 2] photocycloaddition to give metacyclophanes and to discuss its mechanism in comparison with that of paracyclophane synthesis[1].

Preparation of Cyclophanes

Most monomers used were prepared by methods already reported[3]. These are summarized in Scheme 1.

Some results obtained by direct irradiation through a Pyrex filter are summarized in Table 1. *trans*-Cyclophane isomers were not detected in the reaction of **1**, neither by chromatographic nor by spectroscopic analysis. Direct irradiation through a Pyrex filter normally gave satisfactory results. 1,2-Bis(*p*-vinylphenyl)ethane ($n=2$) did not give any cyclophanes at all.

Scheme 1



[a] n = 2: $BrCH_2CH_2OTs$, CuBr/HMPA; $n > 2$: $Br(CH_2)_nBr$, CuBr/HMPA. – [b] CH_3COCl, $AlCl_3$, $ClCH_2CH_2Cl$. – [c] $LiAlH_4$, Et_2O. – [d] $KHSO_4$, DMSO. – [e] HCl, dioxane.

Note that the yields of cyclophanes **2** from α,ω-bis(*p*-vinylphenyl)alkanes **1** depend on the methylene chain length (n). For the cyclization to occur, n must be >2 due to high

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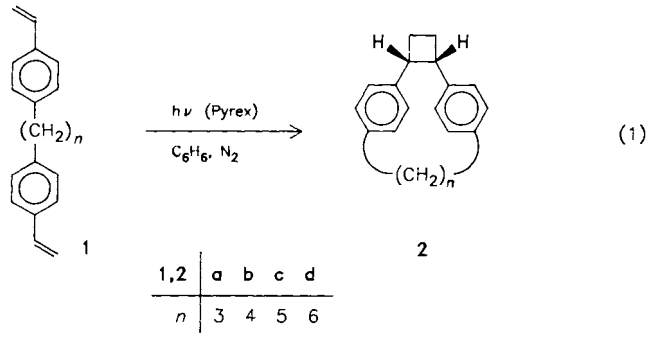
strain build-up in the transition states. When $n = 4$, the cyclophane yield reaches a maximum, and it then decreases as n increases further.

Table 1. Photocyclization of α,ω-bis(vinylphenyl)alkanes **1** and **3**[a]

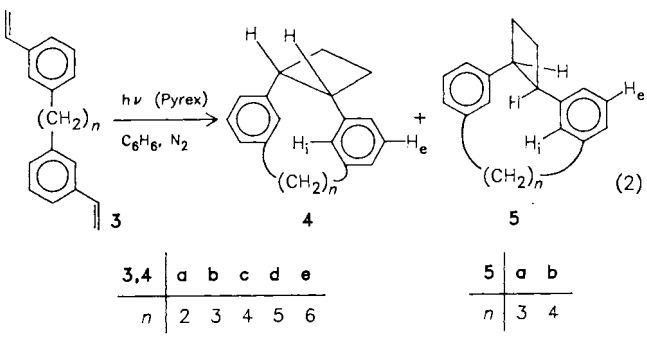
Olefin	Reaction time [h]	Conv. (in %)[b]	Product	Yield (in %)[b,c]	Ratio **4/5**	Ref.
1a ($n=3$)	2.0	25.5	**2a**	13.8	–	[1]
1b ($n=4$)	2.0	40.8	**2b**	60.9	–	[1]
1c ($n=5$)	2.0	40.2	**2c**	48.5	–	[1]
1d ($n=6$)	2.0	25.8	**2d**	trace	–	1
3a ($n=2$)	66.0	–	**4a**	60.9[d]	–	[e]
3b ($n=3$)	18.7	95.3	**4b/5a**	80.4[f]	3.98	[e]
3c ($n=4$)	18.0	96.7	**4c/5b**	70.2[f]	3.88	[e]
3d ($n=5$)	17.0	81.9	**4d**	58.1	–	[e]
3e ($n=6$)	17.0	75.9	**4e**	31.4	–	[e]

[a] Reaction conditions: 400-W high-pressure mercury lamp, Pyrex filter, dry benzene under N_2 at 30°C. – [b] Determined by GC with 1,4-diphenylbutane as an internal standard. – [c] Based on conversion. – [d] Isolated yield. – [e] This work. – [f] Total yield of the two products.

α,ω-Bis(*m*-vinylphenyl)alkanes also gave cyclophanes with a cyclobutane ring as one of the linkages. In contrast to the *para* isomers, these reactions gave the desired product even when $n=2$. Otherwise, the results are similar to those found in the *para* series, except for the formation of *trans* isomers when $n=3$ and 4. The results are also listed in Table 1.



(1)



(2)

Structural Elucidation

According to molecular model examinations, cyclophanes from monomers **1** can only take a *cis* configuration. They show considerably upfield-shifted aromatic proton resonances in the ^{1}H-NMR spectra clearly suggesting a cyclophane structure, and the methine proton signals, characteristic of cyclobutane rings, appear at $\delta \approx 4$, the standard chemical shift for *cis* configuration. NMR data of the characteristic protons are summarized in Table 2.

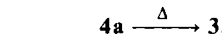
Table 2. ^{1}H-NMR data

Compd.	Chem. shift δ in ppm: Aromatic protons[a]	Methine protons	Δδ	Assignment: This work	Assignment: Reported[b]
2a	6.69–6.17	4.13	–		
2b	6.82–6.37	4.07	–		
2c	6.95–6.53	4.07	–		
2d	7.01–6.60	4.05	–		
4a	7.46–7.04 (4.54, 4.40)	3.98, 3.61	−2.86	*anti*	*anti*
4b	6.90–6.66 (6.55)	4.06	−0.28	*anti*	*anti*
5a	7.36–6.98 (5.49)	2.08	−1.83	*anti*	–
4c	7.06–6.70 (6.46)	3.94	−0.68	*anti*	*anti*
5b	7.33–6.96 (6.01)	1.29	−1.28	*anti*	–
4d	7.01–6.68 (6.87)	4.04	0.08	*syn*	–
4e	7.06–6.70 (6.72)	4.00	−0.29	*anti*	*anti*

[a] Chemical shifts of H_i protons are given in parentheses. – [b] See ref.[4].

When their most stable conformations are taken into consideration, the structures of the metacyclophanes **4** and **5**, obtained from monomers **3**, are rather complicated. Generally speaking, we adopted Lehner's criterion[4] that *anti*-metacyclophanes show negative but large Δδ values ($\Delta\delta = \delta H_i - \delta H_e$; see eq. 2 for the proton designations), while *syn* isomers show positive and small Δδ values. The values are also summarized in Table 2.

Only one product was detected and isolated from the reaction mixture of olefin **3a**. ^{1}H-NMR signals for two nonidentical H_i protons appear at surprisingly high field (δ = 4.54 and 4.40). The high-field shift of these protons clearly shows that the compound is of *anti* conformation. Two nonidentical cyclobutane methine protons are also observed (δ = 3.98 and 3.61). Since the cyclophane displays no *syn/anti* conformational inversion[5], it is therefore of *cis* configuration thus causing a difference of the environments of the two methine protons. Moreover, thermolysis of the cyclophane caused a [2 + 2] cycloreversion to afford olefin **3a** in quantitative yield (eq. 3); Birch reduction of **4a** afforded [2.4]metacyclophane[6]. Note that no *syn* isomer was detected in the photocycloaddition reaction mixture.



(3)

As far as the [2.3]metacyclophanes are concerned, two products, **4b** and **5a** (isomer ratio ca. 4:1), were isolated by column chromatography (benzene/cyclohexane). One product shows a *syn/anti* conformational interconversion on the 200-MHz-NMR time scale, but the other has a rigid skeleton. The former is determined to be **4b**, with *cis* configuration, concluded from the chemical shift of the cyclobutane methine hydrogens (δ = 4.06) as described above. The latter is assigned the *trans* isomer **5a** because of its rigidity and the chemical shift of the methine hydrogens (δ = 2.08), which are much more shielded than those observed in *cis*-cyclophanes **4**. Both cyclophanes have negative $\Delta\delta$ values (see Table 2), and therefore predominantly adopt the *anti* conformation.

The structures and conformations of the [2.4]metacyclophanes **4c** and **5b** were determined as above. The ratio of the major product, **4c** (*anti,cis*), and the minor one, **5b** (*anti,trans*), was ca. 4:1. ^{1}H-NMR spectra of the intraannular aromatic hydrogens (H_i) of **4c** were temperature-independent to −90°C. This is considered to be caused by rapid *syn/anti* interconversion, since only one cyclobutane methine proton signal was observed in the ^{1}H-NMR spectrum of **4c**. The spectra of **5b** were also temperature-independent to −90°C because of the rigid structure of the molecule. **3d** and **3e**, possessing longer methylene chains, afforded **4d** and **4e**, respectively, as the only cyclophane products.

Careful chromatographic and ^{1}H-NMR spectroscopic analyses of the reaction mixtures did not indicate the presence of other isomers. Variable temperature NMR of [2.5]metacyclophane **4d** in [D_6]acetone showed coalescence of the aromatic protons H_i and H_e demonstrating that the compound undergoes *syn/anti*-conformational inversion. The $\Delta\delta$ value clearly indicates that the *syn* conformation is the major one. According to the NMR data ($\Delta\delta$ value, chemical shift of cyclobutane methine protons, etc.), **4e** is *anti,cis*-1,2-ethano[2.6]metacyclophane as depicted in eq. 2.

Irradiation in Several Solvents and in the Presence of Benzophenone (BP) or *p*-Dicyanobenzene (DCNB)

The photochemical additions of **1** and **3** were also studied in the presence of the triplet sensitizer BP. The results are summarized in Table 3.

The sensitizer always increased the *cis/trans* ratio of **4b**/**5a** and accelerated the conversion of the olefins. The same effect was observed when DCNB was added.

The reaction was carried out in several solvents as shown in Table 4. Solvent polarity had only a small effect on the conversion of the olefin and on the product ratio. Most solvents (except ethanol and toluene) gave satisfactory synthetic results.

Stern-Volmer Plot

Logarithmic ratios (Y/Y_0) of cyclophane yields were plotted against the concentration of triethylamine. The experiments were carried out under sufficiently dilute conditions. Cyclophane yields (Y), determined by ^{1}H-NMR spectroscopy, were used for the reactions instead of quantum yields. The plots, depicted in the Figure, show good linear correlations; the $k_q\tau_0$ values are calculated from the slope.

Table 3. Irradiation in the presence of benzophenone (BP) and *p*-dicyanobenzene (DCNB)[a]

Olefin (mM)	Additive (mM)	Conditions: Temp. [°C]; Time [h]	Conv. (in %)[b]	Yield (in %)[b]	Ratio **4b**/**5a**
1a	DCNB	30; 2	29.4	9.5	–
	BP	30; 2	18.2	21.3	–
1b	DCNB	30; 2	56.0	50.3	–
	BP	30; 2	47.3	39.6	–
1c	DCNB	30; 2	50.8	23.0	–
1d	DCNB	30; 2	44.3	28.6	–
3b (7.2)	DCNB (2.8)	40; 8.8	86.1	100	5.6
3b (7.2)	DCNB (6.3)	40; 8.8	91.1	45.4	23.4
3b (7.2)	DCNB (9.0)	40; 8.8	92.5	25.8	22.9
3b (7.2)	BP (3.8)	40; 4.3	75.3	67.3	12.0
3b (7.2)	BP (7.7)	40; 4.3	78.7	49.9	23.6

[a] Through a Pyrex filter. – [b] Determined by gas chromatography, using 1,4-diphenylbutane as an internal standard.

Table 4. Solvent effect on the reaction according to eq. 2[a]

Solvent	ε[b] at 25°C	Conv. (in %)[c]	Yield (in %)[c]	Ratio **4b**/**5a**
acetonitrile	81.6	91.0	84.4	3.6
ethanol	24.55	95.3	62.9	5.6
methylene chloride	8.93	92.7	91.8	6.6
tetrahydrofuran	7.58	89.3	87.7	4.5
toluene	2.38	83.4	74.3	6.3
benzene	2.28	86.6	89.0	3.9
cyclohexane	2.02[d]	84.4	82.7	4.4

[a] Olefin **3b** was irradiated through a Pyrex filter. – [b] Dielectric constant for the pure liquid at 25°C. – [c] Determined by gas chromatography, using 1,4-diphenylbutane as an internal standard. – [d] At 20°C.

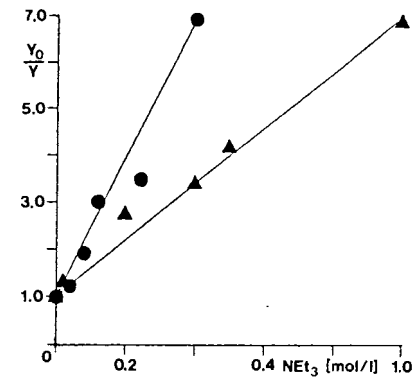


Figure. Stern-Volmer plot of reactions of monomers **1b** (●) and **3b** (▲); $k_q\tau_0$ = 14.1 (for **1b**) and 6.0 (for **3b**).

Discussion

Table 2 compares the most stable conformers of cyclophanes **4** with those of the [*n.m*]metacyclophanes already reported[4]. The good correspondence between them is obvious. Apparently, a cyclobutane ring serving as the cyclo-

phane linkage does not greatly restrict conformational change, provided the junction is *cis*.

On direct irradiation (Pyrex filter, > 280 nm), the solvent effect was not so remarkable as to suggest any polar intermediates in the reaction path. These results are summarized in Table 4.

The addition of BP affected olefin conversion, cyclophane yield, and selectivity of the reaction (eq. 2). The sensitizer generates a triplet excited state from olefins by energy transfer. This triplet state affords a triplet diradical, which has a relatively long lifetime. Within its lifetime, the metacyclophane biradical can change its conformation from the *trans* to the more stable *cis* one. Therefore, the *cis*/*trans* isomer ratio (**4b**/**5a**) is larger in the sensitized reaction.

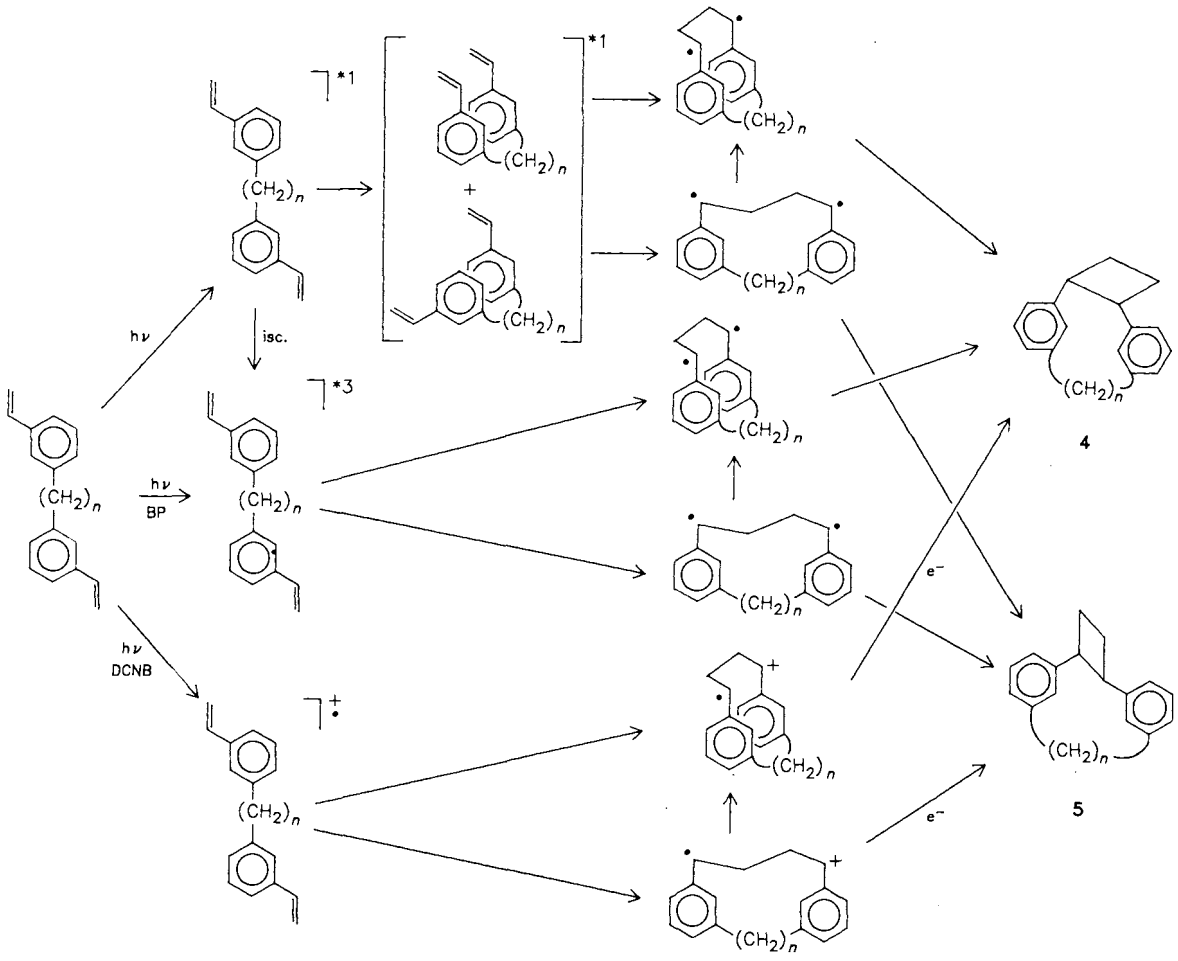
DCNB also affected the cyclization. The higher its concentration, the more olefin was converted, and the higher was the observed *cis*/*trans* selectivity. According to the results previously reported[2], the reaction with the acceptor generates a radical cation species from the styrene moiety, which also has a relatively long lifetime. Therefore, it adopts its most stable conformation, and affords the more stable *cis* cyclophane selectively.

An excimer is often believed to be an important species in the styrene [2 + 2] photocycloaddition, because thermodynamically less stable *cis*-cyclobutanes are produced preferentially[2]. We could not, however, directly observe even the intramolecular excimer emission of **1a**, which satisfies the $n=3$ rule[7]. In the reaction of 1,2-bis(*m*-vinylphenyl)ethane to the *anti*-cyclophane **4a**, an excimer is definitely not involved, because the ethano bridge does not allow the styrene moieties to take up the face-to-face orientation proposed for the excimer. Moreover, the conformtionally less stable *syn* isomer could not be detected in the product mixture.

The Stern-Volmer plot for quenching the reaction with trimethylamine shows a linear correlation and gives $k_q\tau_0 =$ 6.0 for **3b** and 14.2 for **1b**. Since the S_1 state of styrene is known to be quenched by tertiary amines like triethylamine[8], the reaction under direct irradiation is concluded to occur via the S_1 state.

Accordingly, Scheme 2 shows the mechanism for the reaction of *meta*-olefins **3**. The olefin is excited to S_1, which decays to T_1 by intersystem crossing. From the S_1 state, *cis* and *trans* singlet diradicals are generated. Both *cis* and *trans* diradicals can give cyclophanes **4** and **5**, when $n=3$ and 4. If the initially formed cyclic diradical has a ring system large enough to allow the aromatic ring to rotate, it changes its conformation from the thermodnamically unstable *trans* diradical form to the stable *cis* one. In fact, **3d** and **3e** ($n \geq 5$) gave only the *cis*-cyclophanes **4d** and **4e**.

Scheme 2



The mechanism of the reaction of olefin **1** is considered to be almost the same as that shown in Scheme 2, but the cyclization step towards the *trans*-cyclophane is strictly forbidden because of the high strain energy involved.

Experimental

Elemental analyses were performed at the Microanalysis Center of Kyoto University. – Melting points are not corrected. – NMR spectra were recorded on a Varian XL-200 FT-NMR spectrometer. – Mass spectra were recorded on a Hitachi M-80A mass spectrometer. – High performance liquid chromatographic analyses (HPLC) were carried out using Altex Model 100A and Knauer 64 pumps with a Hitachi wavelength-tunable effluent monitor and a Shimadzu SPD-6A UV spectrophotometric detector. – Gas chromatographic analyses were performed with a Shimadzu GC-4C IT gas chromatograph. – Solvents and triethylamine were purified by the reported methods[9]. Other commercially available highest grade reagents were used without further purification. Monomers were conveniently prepared by the methods reported previously[3].

1) *Intramolecular [2 + 2] Photocycloaddition (General Procedure):* 1,4-Bis-(*m*-vinylphenyl)butane[4] (**3c**, 637 mg, 2.43 mmol) was irradiated in dry and N_2-degassed benzene (400 ml) under N_2 using a 400-W high-pressure mercury lamp with a Pyrex filter. After 18 h, the reaction mixture was concentrated by evaporation and treated with an excess of diborane in THF to convert any unconsumed monomer into more polar material with higher molecular weight; *cis*- and *trans*-1,2-ethano[2.4]metacyclophane (**4c** and **5b**) were easily isolated by column chromatography (SiO_2, cyclohexane/benzene). Yields are listed in Table 1. Physical and analytical data of the cyclophanes obtained are summarized in Table 5. ^{1}H-NMR data are listed in Table 6.

Table 5. Physical and analytical data of the cyclophanes

Compd.	Mp [°C]	C/H Analysis Calcd. (Found)	MS (*m/z*, M^+) Calcd. (Found)
2a	136–137	91.88(91.74)/8.12(8.26)	248.1566(248.1566)
2b	102–103	91.55(91.46)/8.45(8.49)	262.1723(262.1725)
2c	128–129	91.25(91.03)/8.75(8.87)	276.1879(276.1872)
2d	81–82	90.98(90.68)/9.02(9.26)	290.2036(290.2036)
4a	78–80	92.26(92.20)/7.74(7.80)	234.1409(234.1408)
4b	61–62		248.1566(248.1561)
4c	oil		262.1723(262.1726)
4d	70–71	91.25(90.95)/8.75(8.86)	276.1879(276.1883)
4e	oil		290.2072(290.2023)
5a	113–116		248.1566(248.1557)
5b	69–70	91.55(91.32)/8.45(8.68)	262.1723(262.1724)

2) *Irradiation in the Presence of Additives:* Samples were prepared in test tubes. Olefin **3b** and an additive were dissolved in benzene to the prescribed concentrations under N_2 (see Table 3), and degassed by cycles of freeze-thawing. The test tube was then sealed and placed in a merry-go-round apparatus at a distance of 6 cm from the light source. After irradiation for the prescribed period, the mixture was concentrated by evaporation. The prescribed amount of trimethylphenylsilane as a standard (ca. 5 mole % with respect to the olefin) was added to the mixture, which was then analyzed by 200-MHz ^{1}H-NMR spectroscopy.

3) *Quenching Experiment with Triethylamine:* Samples were prepared in test tubes. Olefin **3b** and triethylamine were placed in a test tube, dissolved in benzene (10 ml) to the prescribed concentrations ([**3b**] = 0.025 mol/l; [NEt_3] = 0.0–1.0 mol/l) under N_2, and degassed by cycles of freeze-thawing. The test tube was then sealed and placed in a merry-go-round apparatus at a distance of 6 cm from the light source. After 2 h of irradiation, the mixture was concentrated by evaporation, combined with the prescribed amount of trimethylphenylsilane as a standard (ca. 1 mole % with respect to the olefin), and analyzed by 200-MHz ^{1}H-NMR spectroscopy.

Table 6. ^{1}H-NMR Data of the cyclophanes[a]

Compd.	Chemical shift δ (multiplicity *J* [Hz])
2a	6.66 (*A*Bq, 8.0, 1.8, 2H), 6.59 (A*B*q, 8.0, 1.8, 2H), 6.51 (*A*Bq, 7.7, 1.6, 2H), 6.20 (A*B*q, 7.7, 1.6, 2H), 4.13 (m, 2H), 2.71 (t, 5.7, 4H), 2.50 (m, 4H), 2.12 (m, 2H).
2b	6.79 (*A*Bq, 8.0, 1.8, 2H), 6.61 (A*B*q, 8.0, 1.8 2H), 6.52 (*A*Bq, 7.7, 1.8, 2H), 6.40 (A*B*q, 7.7, 1.8, 2H), 4.07 (m, 2H), 2.49 (m, 4H), 2.27 (br. s, 2H), 1.47 (br. s, 2H).
2c	6.92 (*A*Bq, 7.8, 1.6, 2H), 6.71 (A*B*q, 7.8, 1.6, 2H), 6.63 (*A*Bq, 7.6, 1.6, 2H), 6.56 (A*B*q, 7.6, 1.6, 2H), 4.07 (m, 2H), 2.51 (m, 4H), 2.38 (t, 6.1, 4H), 1.33 (m, 5H), 0.40 (m, 1H).
2d	6.98 (*A*Bq, 7.9, 1.8, 2H), 6.79 (A*B*q, 7.9, 1.8, 2H), 6.71 (*A*Bq, 7.8, 1.8, 2H), 6.63 (A*B*q, 7.8, 1.8, 2H), 4.05 (m, 2H), 2.46 (m, 8H), 1.42 (m, 5H), 0.67 (quint, 3.2, 3H).
4a	7.42 (t, 7.2, 1H), 7.37 (d, 4.0, 1H), 7.24 (t, 7.3, 1H), 7.09 (m, 3H), 4.54 (s, 1H), 4.40 (s, 1H), 3.98 (dt, 11.6, 7.5, 1H), 3.59 (m, 1H), 3.14 (m, 2H), 2.41 (m, 2H), 1.81 (m, 4H).
4b	6.85 (t, 4.4, 2H), 6.70 (d, 8.4, 2H), 6.55 (br. s, 4H), 4.06 (s, 2H), 2.76 (br. s, 4H), 2.43 (d, 4.0, 4H), 1.89 (br. s, 2H).
4c	7.05 (t, 7.4, 2H), 6.96 (dt, 7.6, 1.6, 2H), 6.77 (dt, 7.2, 1.6, 2H), 6.37 (s, 2H), 3.94 (tt, 5.1, 2.5, 2H), 2.45 (br. t, 5.4, 4H), 2.38 (t, 3.7, 4H), 1.41 (quint, 3.0, 4H).
4d	6.97 (t, 7.5, 2H), 6.87 (s, 2H), 6.81 (dt, 7.6, 1.4, 2H), 6.71 (dt, 7.4, 1.4, 2H), 4.04 (tt, 5.2, 2.6, 2H), 2.54 (m, 8H), 1.61 (quint, 7.0. 4H), 0.58 (dsept, 3.6, 7.3, 2H).
4e	7.01 (t, 7.5, 2H), 6.86 (dt, 7.6, 1.4, 2H), 6.76 (dt, 7.4, 1.4, 2H), 6.71 (s, 2H), 3.99 (tt, 5.2, 2.5, 2H), 2.47 (m, 8H), 1.57 (m, 4H), 0.90 (quint, 3.1, 4H).
5a	7.31 (t, 7.5, 2H), 7.08 (d, 7.6, 2H), 7.02 (d, 7.0, 2H), 5.48 (s, 2H), 2.76 (m, 4H), 2.40 (m, 4H), 2.08 (m, 2H), 1.97 (m, 2H).
5b	7.29 (t, 7.4, 2H), 7.14 (d, 7.8, 2H), 6.99 (d, 7.2, 2H), 6.01 (s, 2H), 2.77 (m, 4H), 2.36 (m, 4H), 2.09 (m, 2H), 1.66 (m, 2H), 1.29 (m, 2H).

[a] Taken in $CDCl_3$ on a Varian XL-200 NMR spectrometer, using TMS as an internal standard.

CAS Registry Numbers

1a: 58845-03-7 / **1b**: 41996-99-0 / **1c**: 79541-69-8 / **1d**: 32927-54-1 / **2a**: 116559-78-5 / **2b**: 116559-79-6 / **2c**: 116559-80-9 / **2d**: 116559-81-0 / **3a**: 116467-70-0 / **3b**: 107270-48-4 / **3c**: 107270-49-5 / **3d**: 107270-50-8 / **3e**: 107270-51-9 / **4a**: 116467-65-3 / **4b**: 116467-66-4 / **4c**: 116467-67-5 / **4d**: 116467-68-6 / **4e**: 116467-69-7 / **5a**: 116559-82-1 / **5b**: 116559-83-2

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