[2.2]Naphthalenophanes from Intermolecular [2 + 2] Photocycloadditions of Divinylnaphthalenes

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syn-[2.2]Naphthalenophanes were obtained exclusively in reasonable yields from the intermolecular [2 + 2] photocycloadditions of divinylnaphthalenes. The position of the vinyl group and the type of vinyl substituent affected the isomer ratio of the products. The structures of naphthalenophanes were elucidated by ^{1}H-NMR spectroscopy including COSY and NOESY experiments. Among the divinylnaphthalenes examined, 1,4-, 1,5-, and 1,6-ones did not give the desired naphthalenophanes. By taking advantage of the effect of the substituents on the photoreaction, we could obtain [2.2]-(1,5)naphthalenophane derivatives from 1,5-bis(β-carbethoxyethenyl)naphthalene and 1,5-bis(β-phenylethenyl)naphthalene, but we could not obtain the 1,4-isomers, probably because they are highly strained. Although a mixture of two different divinylnaphthalenes was irradiated, only homo-adducts were obtained; no cross adducts were detected.

[2.2]Naphthalenophanes, highly strained compounds that are difficult to synthesize, were first synthesized in 1951 by Baker and co-workers. They used a sodium- or phenyllithium-induced benzylic coupling of 2,7-bis(bromomethyl)naphthalene.[1] Since their report, a considerable number of investigations have appeared on the chemistry of [2.2](1,4)naphthalenophanes, which undergo interesting isomerizations and intramolecular rotations of the naphthalene rings. The anti isomer, first reported in 1963, was formed by a dimerization of a benzo-*p*-xylylene intermediate generated *in situ* from an appropriate ammonium salt.[2] A highly efficient synthesis of [2.2](1,4)-naphthalenophanes by means of elimination of an appropriate tosylate has also been reported.[3] Other naphthalenophanes, such as [2.2](1,5)- and [2.2](2,6)-ones, were prepared by sulfur extrusion of SO_2 from the corresponding disulfones, which were obtained by the oxidation of dithianaphthalenophanes. They were obtained as mixtures of *achiral-* and *chiral*-ones.[4] None of the methods reported previously, however, afforded syn isomers exclusively.

Although many bis(vinylnaphthyl)alkanes give [2.*n*]-naphthalenophanes by means of efficient intramolecular [2 + 2] photocycloaddition,[5] [2.2]naphthalenophanes cannot be obtained by this intramolecular reaction, probably because of the conformational difficulty of getting the two vinyl moieties close together in the *trans*-1,2-disubstituted ethane conformer, which is generally the major conformer. If one could orient the two vicinal vinyl moieties in the same direction by using a ring system such as cyclobutane, the [2 + 2] photocycloaddition of these vinyl moieties might afford another two-carbon linkage as the cyclobutane ring. Some [2.2]cyclophanes have already been successfully synthesized by the intermolecular [2 + 2] photocycloadditions of the appropriate di- and trivinylbenzenes.[6,7] Accordingly, we were prompted to investigate the use of intermolecular [2 + 2] photocycloadditions of divinylnaphthalenes for the synthesis of [2.2]naphthalenophanes. In this paper, we would like to report the effect of the position of the vinyl group and the nature of the vinyl substituents on this photocycloaddition, the structural elucidation by NMR spectroscopy, and the results of competitive intermolecular [2 + 2] photocycloadditions.

Preparation of Divinylnaphthalenes and Their Derivatives. Divinylnaphthalenes have themselves attracted much attention in terms of their spectroscopic properties,[8] conformations,[9] polymerization reactions,[10] photoreactions,[9,11] thermal reactions,[12] and their applications to the syntheses of naphthoquinodimethanes.[11] Several divinylnaphthalenes, such as 1,2-,[9] 1,5-,[10,14,15] 1,8-,[9,15,16] 2,3-,[9,13] and 2,6-ones,[17] have been prepared previously.

The palladium-catalyzed cross coupling reaction of aryl bromides and triflates with tri-*n*-butylethenylstannane is frequently used in preparative organic chemistry.[18] We applied this reaction to the preparation of divinylnaphthalenes and their derivatives (see Scheme I) because high regioselectivity is expected and most of the starting materials are commercially available. Since their photoreaction had already been reported in detail,[9,11] 1,2- and 1,8-divinylnaphthalenes were not prepared.

The coupling reactions of bis((trifluoromethyl)sulfonyl)-naphthalenes 2 with tri-*n*-butylethenylstannane in the

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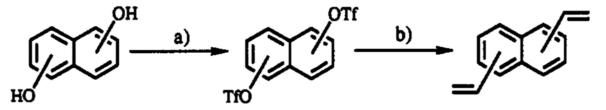
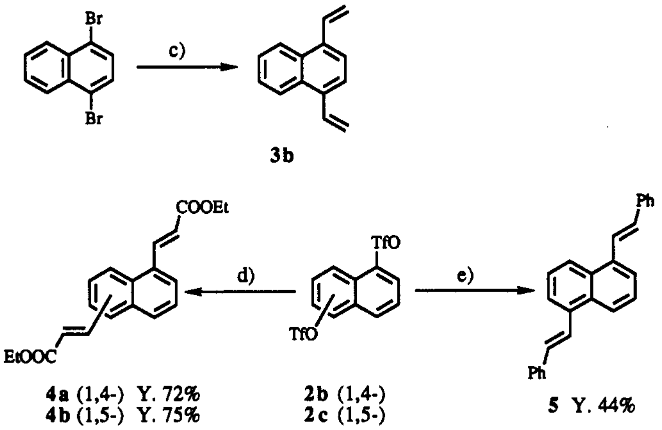
Scheme I. Preparation of Divinylnaphthalenes[a]



Compd	Position		
1a	1,3-	2a	3a
1b	1,4-	2b	3b
1c	1,5-	2c	3c
1d	1,6-	2d	3d
1e	1,7-	2e	3e
1f	2,3-	2f	3f
1g	2,6-	2g	3g
1h	2,7-	2h	3h



3b

4a (1,4-) Y. 72%
4b (1,5-) Y. 75%

2b (1,4-)
2c (1,5-)

5 Y. 44%

[a] Key: (a) $(CF_3SO_2)_2O$/pyridine; (b) $(n\text{-}Bu)_3SnCH{=}CH_2$, LiCl, $(Ph_3P)_4Pd$/dioxane; (c) $(n\text{-}Bu)_3SnCH{=}CH_2$, $(Ph_3P)_4Pd$/toluene; (d) $CH_2{=}CHCOOEt$, Et_3N, $(Ph_3P)_2PdCl_2$/DMF; (e) $CH_2{=}CHPh$, Et_3N, $(Ph_3P)_2PdCl_2$/DMF.

presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) afforded divinylnaphthalenes **3**. In most cases, yields were excellent. The 1,4- and 1,5-bis(β-carbethoxyethenyl)naphthalenes and 1,5-bis(β-phenylethenyl)naphthalene were also synthesized by this kind of substitution.

Triflates **2** were made by the treatment of commercially available dihydroxynaphthalenes **1** with trifluoromethanesulfonic anhydride.[19] All triflates were obtained in good yields (63–89%) and in high purity as indicated by TLC analysis and their sharp melting points.

Triflates **2** readily reacted with tri-*n*-butylethenylstannane in the presence of tetrakis(triphenylphosphine)palladium(0) to form divinylnaphthalenes **3** in reasonable yields (74–86%).[19] Their structures were determined by ^{1}H NMR spectroscopy. 1,4-Dibromonaphthalene, prepared by quantitative bromination of naphthalene or 1-bromonaphthalene, could be used instead of triflate **2b** in this coupling reaction.[20] The yield with the bromide was the same as that with **2b**.

Substituted olefins, 1,4- and 1,5-bis(β-carbethoxyethenyl)naphthalenes **4**, and 1,5-bis(β-phenylethenyl)naphthalene (**5**) were prepared from the appropriate triflates, ethyl acrylate, or styrene in the presence of bis(triphenylphosphine)palladium(II) chloride.

Photoreactions of Divinylnaphthalenes. In 1970, Meinwald and his co-workers reported the photoreactions of 1,2- and 1,8-divinylnaphthalenes.[9] Upon irradiation in rather dilute solution, 1,2-divinylnaphthalene underwent intramolecular photocycloaddition between the neighboring vinyl groups to give phenanthrene derivatives.[9] 1,8-Divinylnaphthalene also gave predominantly intramolecular cycloaddition products, again under dilute conditions.[9,11]

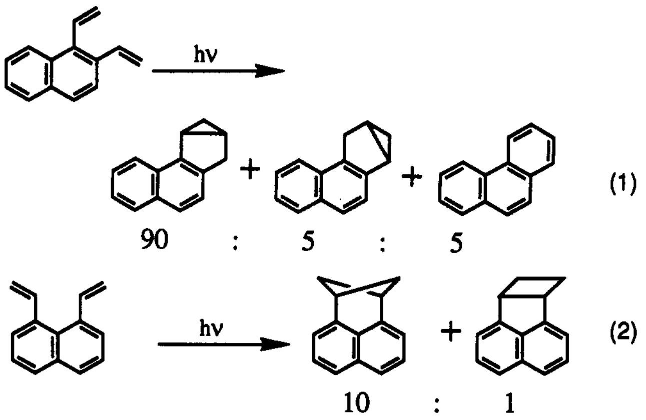


Table I. Preparation of Naphthalenophanes[a]

entry	olefin			product[b]	yield, %	cyclobutane confign[c]
		R	position			
1	3a	H	1,3	6a	8	exo,endo (100)
2	3b[d]	H	1,4	6b	0	
3	3c[d]	H	1,5	6c	0	
4	3d[d]	H	1,6	6d	0	
5	3e	H	1,7	6e	15	exo,endo (65), exo,exo (35)
6	3f	H	2,3	6f	18	endo,endo (100)
7	3g	H	2,6	6g	20	mixture (50:50)
8	3h	H	2,7	6h	27	endo,endo (65), exo,endo (35)
9	4a[d]	COOEt	1,4	7a	0	
10	4b	COOEt	1,5	7b	47	exo,exo (100)
11	5	Ph	1,5	8	42	exo,exo (100)

[a] Reaction conditions: olefin (0.1 M) in benzene through Pyrex filter with a 400-W high-pressure mercury lamp. [b] ^{1}H NMR data and analytical data of the products are available in Tables II and Table VI, respectively. [c] Isomer ratios are given in parentheses. [d] No naphthalenophanes were obtained.

The photoreactions of divinylnaphthalenes **3a**–**3h** were carried out under conditions similar to those used for the intramolecular [2 + 2] photocycloaddition mentioned above. Upon irradiation, 1,3- (**3a**), 1,7- (**3e**), 2,3- (**3f**), 2,6- (**3g**), and 2,7-divinylnaphthalenes (**3h**) gave the corresponding [2.2]naphthalenophanes **6a**, **6e**, **6f**, **6g**, and **6h**, respectively. The 1,4- (**3b**), 1,5- (**3c**), and 1,6-divinylnaphthalenes (**3d**) gave not [2.2]naphthalenophanes but polymeric material. Although no mechanistic work has been done yet, this photocycloaddition is believed to occur stepwise because half-cyclized products have often been observed in several reaction mixtures.[6] In this work, we would like to discuss the photochemical synthesis of [2.2]naphthalenophanes.

The structures of naphthalenophanes were elucidated by NMR spectroscopy, including COSY and NOESY experiments, as described below.

The photoproduct of **3a** was determined to have the *exo,endo,syn*-[2.2](1,3)naphthalenophane structure **6a**. All of the aromatic protons in **6a** resonate at higher field than those of naphthalene itself (Table II). Moreover, no extremely high-field protons, which would be expected for anti-isomers, were observed. From the NOESY experiment, interactions were detected between the cyclobutane methine protons and the aromatic C8 protons

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(19) Results are available in the supplementary material.

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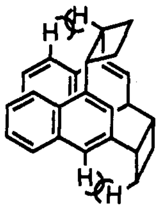
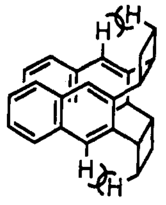
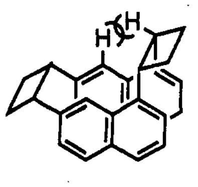


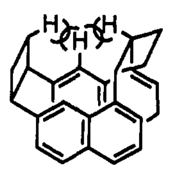
6a



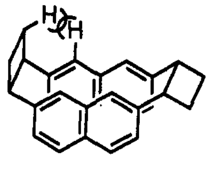
6f



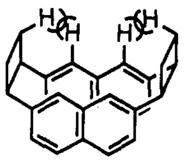
exo,exo-**6e**
minor



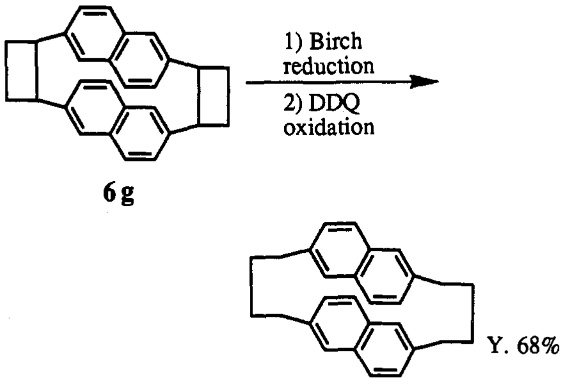
exo,endo-**6e**
major



exo,endo-**6h**
minor



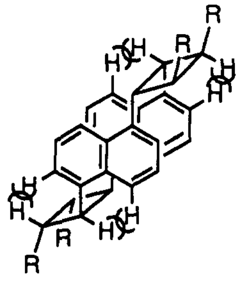
endo,endo-**6h**
major



6g

[4.4](2,6)Naphthalenophane

(3)



7b (R = COOEt)
8 (R = Ph)

and between the cyclobutane methylene protons and the aromatic C4 protons (see Table III). Although the exo-conformational rigidity of its α-vinyl group has been proved,[5] our result suggests that the corresponding conformation of the vinyl groups of **3a** is predominant and that the cyclization occurs via this conformer. The same conformational preference has already been invoked for the photoreaction of *m*-divinylbenzene.[6]

Divinylnaphthalene **3f**, like **3a**, gave the *endo,endo,syn*-[2.2](2,3)naphthalenophane (**6f**) as the sole cycloaddition product in 18% yield. None of the aromatic protons of **6f** resonate at extremely high-field (see Table II), and an NOE interaction was observed between the cyclobutane methylene protons and the peri protons (C1 and C4 protons) (see Table III). Accordingly, naphthalenophane **6f** is concluded to have the syn-conformation and *endo,endo*-cyclobutane configuration as shown. The major conformation of **3f** is expected to be the *endo,endo*-one because of the severe steric interaction between the two methylene groups. The present experimental evidence confirms this conformational preference of **3f**.

On the other hand, the photoreaction of **3e** gave a mixture of two isomeric *syn*-[2.2](1,7)naphthalenophanes **6e** in a ratio of 65:35. The components were separated by preparative HPLC (reversed phase, C-18, methanol). According to the ^{1}H NMR spectra (see Table II), the two isolated compounds are also of the syn-conformation because their aromatic protons resonate at higher field than those of naphthalene itself, and no extremely high-field protons, expected for the anti-isomers, are observed. In the major product, an NOE interaction was detected between the cyclobutane-methine and -methylene protons and the C8 protons. In the minor product, an NOE interaction was observed between the cyclobutane methine protons and the C8 protons. Accordingly, the structures of the major and minor products are concluded to be *exo,endo*-**6e** and *exo,exo*-**6e**, respectively.

The photoreaction of **3h** was similar to that of **3e** and gave a mixture of two isomeric *syn*-[2.2](2,7)naphthalenophanes **6h** in 27% yield in a ratio of 65:35. The mixture was separated by HPLC (reversed phase, C-18, methanol). According to the ^{1}H NMR spectra (see Table II) and the NOESY experiment, the structures of the major and minor products were determined to be *endo,endo*-**6h** and *exo,endo*-**6h**, respectively.

Upon irradiation, 2,6-divinylnaphthalene (**3g**) formed a mixture of isomeric [2.2](2,6)naphthalenophanes **6g**, but the mixture could not be separated by column chromatography, HPLC, solvent extraction, or recrystallization from common solvents. Therefore, the isomer mixture of **6g** was converted to [4.4](2,6)naphthalenophane[5] by means of a Birch reduction and a subsequent DDQ oxidation (see Experimental Section). The yield was 68%. This result confirms the formation of [2.2](2,6)naphthalenophanes **6g** from the [2 + 2] photocycloaddition of 2,6-divinylnaphthalene (**3g**).

Photoreaction of Divinylnaphthalene Derivatives. The photoreactions of divinylnaphthalenes, bis(β-carbethoxyethenyl)naphthalenes (**4**), and 1,5-distyrylnaphthalene (**5**) were carried out under the same conditions mentioned above (see Table I).

The attempted photoreaction of 1,5-divinylnaphthalene (**3c**) did not give any [2.2](1,5)naphthalenophanes **6c**, whereas derivatives **4b** and **5** formed *syn*-[2.2](1,5)-naphthalenophane derivatives **7b** and **8**, respectively, in reasonable yields (42–47%). Since carboalkoxyl and phenyl groups attached to 1,3-bis(vinylnaphthyl)propane have been reported to promote the [2 + 2] photocyclo-

Table II. ^{1}H NMR Spectroscopic Data of [2.2]Naphthalenophane Derivatives[a]

product	^{1}H NMR (CDCl$_3$/TMS), δ (intensity, multiplicity, coupling constant, assignment)
6a	7.55 (2H, m, C8-H), 7.26 (2H, m, C5-H), 6.97 (2H, d, $J = 1.6$ Hz, C4-H), 6.91 (4H, m, C6- and C7-H's), 6.82 (2H, d, $J = 1.6$ Hz, C2-H), 5.28 (2H, m, C1-methine), 4.49 (2H, m, C3-methine), 2.62 (8H, m, methylene)
exo,exo-**6e** and *exo,endo*-**6e**	7.88 (2H, d, $J = 1.6$ Hz, C8-H), 7.26 (2H, d, $J = 8.2$ Hz, C5-H), 7.20 (2H, bd, $J = 7.8$ Hz, C4-H), 7.16 (2H, bd, C2-H), 7.04 (2H, t, $J = 7.6$ Hz, C3-H), 6.94 (2H, dd, $J = 1.6$ Hz, C6-H), 5.12 (2H, m, C1-methine), 4.46 (2H, m, C3-methine), 2.67 (8H, m, methylene)
	8.30 (2H, d, $J = 1.6$ Hz, C8-H), 7.13 (8H, m, C2-, C3-, C4-, and C5-H's), 6.64 (2H, dd, $J = 8.3$ and 1.6 Hz, C6-H), 5.28 (2H, m, C1-methine), 4.30 (2H, m, C7-methine), 2.80 (8H, m, methylene)
6f	7.61 (4H, m, C5- and C8-H's), 7.41 (4H, s, C1- and C4-H's), 7.24 (4H, m, C6- and C7-H's), 4.22 (4H, m, methine), 2.67 (8H, m, methylene)
exo,endo-**6h**	7.31 (2H, d, $J = 1.6$ Hz, C8-H), 7.06 (2H, d, $J = 1.6$ Hz, C1-H), 7.04 (2H, d, $J = 8.2$ Hz, C4-H), 6.91 (2H, d, $J = 8.2$ Hz, C5-H), 6.84 (2H, dd, $J = 8.2$ and 1.6 Hz, C3-H), 6.44 (2H, dd, $J = 8.2$ and 1.6 Hz, C6-H), 4.30 (4H, m, methine), 2.63 (8H, m, methylene)
endo,endo-**6h**	7.43 (4H, d, $J = 2.0$ Hz, C1- and C8-H's), 6.87 (4H, d, $J = 8.6$ Hz, C4- and C5-H's), 7.61 (4H, dd, $J = 8.6$ and 2.0 Hz, C3- and C6-H's), 4.29 (4H, m, methine), 2.70 (8H, m, methylene)
7b	7.48 (4H, d, $J = 7.6$ Hz, C4- and C8-H's), 6.83 (4H, d, $J = 7.7$ Hz, C2- and C6-H's), 6.57 (4H, d, $J = 7.0$ Hz, C3- and C7-H's), 5.22 (4H, d, $J = 5.9$ Hz, Nap-C*H*), 4.32 (8H, q, $J = 5.1$ Hz, COOC*H*$_2$CH$_3$), 4.01 (4H, d, $J = 5.9$ Hz, C*H*COOEt), 1.37 (12H, t, $J = 5.1$ Hz, COOCH$_2$C*H*$_3$)
8	7.54 (4H, m, C4- and C8-H's), 7.36–7.10 (20H, m, Ph-H's), 6.90 (8H, m, C2-, C3-, C6-, and C7-H's), 5.25 (4H, d, $J = 6.2$ Hz, Nap-C*H*), 4.69 (4H, d, $J = 6.2$ Hz, C*H*Ph)

[a] Since naphthalenophane **6g** could not be separated, any detailed ^{1}H NMR analysis has not been done.

Table III. NOE Interactions between Cyclobutane Protons and Aromatic Protons of Naphthalenophanes 6–8

[2.2](m,n)-naphthalenophane			Cn-cyclobutane		Cm-cyclobutane	
compd	m	n	benzyl	phenethyl	benzyl	phenethyl
6a	1	3	C8-H			C4-H
exo,exo-**6e**	1	7	C8-H			
exo,endo-**6e**	1	7	C8-H			C8-H
6f	2	3		C1-H		C4-H
exo,endo-**6h**	2	7				C8-H
endo,endo-**6h**	2	7		C1-H		C8-H
7b	1	5	C8-H	C2-H	C4-H	C6-H
8	1	5	C8-H	C2-H	C4-H	C6-H

addition,[21] we believe that this result is also due to the facilitation of the photocycloaddition probably by stabilization of excited state, which makes the lifetime longer and facilitates the second cyclization, or by suppression of rapid side reactions like polymerization, which is possible for the vinylnaphthalene moiety but not for the β-substituted one.

The structures of naphthalenophanes **7b** and **8** were elucidated by ^{1}H NMR spectroscopy, including COSY and NOESY experiments (see Table III and Figure 1). The ^{13}C NMR spectra of **7b** and **8** are listed in Table IV. From the NOESY experiment, interactions were observed between the cyclobutane benzylmethine protons and the aromatic C8 protons and also between the cyclobutane phenethylmethine protons and the aromatic C2 protons. Hence, the structures of **7b** and **8** were determined to be those depicted above.

1,4-Bis(β-carbethoxyethenyl)naphthalene (**4a**), however, did not give the corresponding naphthalenophanes **7a**, even though it was irradiated under the modified conditions and its gradual consumption was observed. This result is probably due to the strain of the desired naphthalenophanes, which is higher than that of 1,5-isomer **7b**.

Competitive Photoreaction of Divinylnaphthalenes. A mixture of divinylnaphthalenes was irradiated in order to obtained a new type of naphthalenophanes, *e.g.*, [2.2](1,6)(1,7)-, [2.2](1,7)(2,7)-, [2.2](2,6)(2,7)-ones, *etc.* The 1:1 mixture of two different divinylnaphthalenes was irradiated under the same conditions as above (see Table V). In all cases, no cross adducts were formed; only homoadducts were obtained. The naphthalenophane formation was monitored by ^{1}H NMR spectroscopy. Generally speaking, one naphthalenophane from the homocoupling of an olefin appeared first (the first product in Table V), and after the complete consumption of the olefin, a second naphthalenophane from another olefin appeared (the second one in Table V). From the data in Table V, the reactivity of divinylnaphthalenes is concluded to decrease in the order of 2,3 (**3f**) > 1,3 (**3a**), 2,7 (**3h**) > 2,6 (**3g**) > 1,7 (**3e**); the reactivity of carbethoxy substituted (**4b**) > phenyl substituted (**5**). This order is believed to arise from the photoreactivities of olefins; the strain energy differences come into play at the transition state. At this time, a relationship has not been established between the naphthalenophane-strain energies and the photoreactivities.

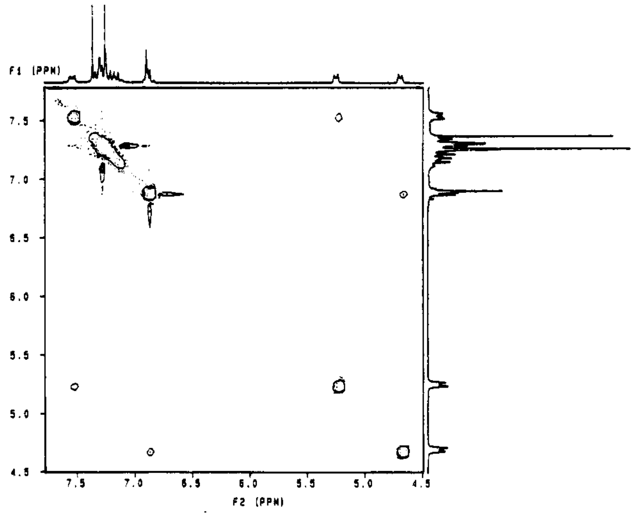


Figure 1. NOESY spectrum of naphthalenophane 8.

Table IV. ^{13}C NMR Spectroscopic Data of [2.2]Naphthalenophane Derivatives 7b and 8

product	^{13}C NMR (CDCl$_3$/TMS), δ
7b	172.8 (2C), 134.0 (2C), 132.4 (2C), 124.9 (2C), 124.4 (2C), 121.7 (2C), 61.2 (2C), 44.5 (2C), 41.2 (2C), 14.3 (2C)
8	141.5 (2C), 135.8 (2C), 132.7 (2C), 128.3 (4C), 128.1 (4C), 125.9 (2C), 124.8 (2C), 124.4 (2C), 121.4 (2C), 48.5 (2C), 44.6 (2C)

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[21] Nishimura, J.; Takeuchi, M.; Takahashi, H.; Sato, M. *Tetrahedron Lett.* **1990**, *31*, 2911 and references cited therein.

Table V. Photoreaction of Mixed Divinylnaphthalenes[a]

divinylnaphthalenes	first product	second product
3a and **3b**	**6a**	
3a and **3f**	**6f**	**6a**
3b and **3f**	**6f**	
3b and **4a**[b]		
3c and **3d**[b]		
3c and **3e**	**6e**	
3c and **3g**	**6g**	
3c and **3h**	**6h**	
3c and **4b**	**7b**	
3c and **5**	**8**	
3d and **3e**	**6e**	
3d and **3g**	**6g**	
3d and **3h**	**6h**	
3e and **3g**	**6g**	**6e**
3e and **3h**	**6h**	**6e**
3g and **3h**	**6h**	**6g**
4b and **5**	**7b**	**8**

[a] Reaction conditions: olefins (each of 0.1 mmol) in benzene-d_6 (1 mL) through Pyrex filter with a 400-W high-pressure mercury lamp. [b] No naphthalenophanes were obtained.

Table VI. Physical and Analytical Data of Naphthalenophanes 6–8

product	mp, °C	found C/H, %	calcd C/H, %
6a	211–212	93.03/6.93	93.29/6.71
exo,exo-**6e**	>300		
		93.02/6.90[a]	93.29/6.71
exo,endo-**6e**	>300		
6f	269–271	93.04/6.89	93.29/6.71
6g	>300	93.13/6.84[a]	93.29/6.71
exo,endo-**6h**	>300		
		93.14/6.83[a]	93.29/6.71
endo,endo-**6h**	>300		
7b	>300	74.00/5.99	74.06/6.21
8	>300	93.83/6.16	93.94/6.06

[a] Naphthalenophanes **6e**, **6g**, and **6h** were determined as the isomer mixture.

Experimental Section

General Methods. NMR spectra were recorded in $CDCl_3$ solution on a Varian Gemini-200 FT NMR spectrometer. HPLC analysis was performed with a Shimadzu LC-6A pump, an LC-6A UV detector, and an RC4A data processor. Melting points are not corrected.

Materials. Benzene and toluene were purified by refluxing over Na and distilling from Na under a nitrogen atmosphere. Other commercially available reagents were used without further purification, unless otherwise noted.

1,5-Naphthyl Bis(trifluoromethanesulfonate) (2c). General Procedure.[18] To a solution of 1,5-dihydroxynaphthalene (**1c**) (0.32 g, 2.0 mmol) in pyridine (4 mL) at 0 °C was slowly added trifluoromethanesulfonic anhydride (1.24 g, 4.4 mmol). The reaction mixture was stirred at 0 °C for 5 min and then allowed to warm to rt for 24 h. The mixture was poured into water and extracted with benzene (3 × 20 mL). The benzene extract was washed sequentially with 10% aqueous hydrochloric acid (two times), water, and saturated aqueous sodium chloride and then dried over $MgSO_4$ and evaporated. Column chromatography (SiO_2, hexane) afforded triflate **2c** as colorless crystals (0.61 g, 76%).

1,5-Divinylnaphthalene (3c). General Procedure.[18] To a solution of triflate **2c** (0.80 g, 2.0 mmol) in 1,4-dioxane (20 mL) were added tri-*n*-butylethenylstannane (1.4 g, 4.4 mmol),[14] LiCl (0.51 g, 12 mmol), tetrakis(triphenylphosphine)palladium(0) (92 mg, 80 μmol), and a few crystals of 4-*tert*-butylcatechol as a radical inhibitor. The resulting suspension was heated to reflux for 4 h, cooled to rt, filtered, concentrated, and then diluted with ether. The ether solution was treated with 20% aqueous KF solution (2.0 mL) and stirred vigorously for 30 min. The ether phase was decanted from solid tin fluoride polymer and the aqueous phase, and then the solvent was removed. The residue was purified by column chromatography (SiO_2, hexane) to afford 1,5-divinylnaphthalene (**3c**) as colorless crystals (0.31 g, 75%).

1,5-Bis(*trans*-β-carbethoxyethenyl)naphthalene (4b). General Procedure. To a solution of triflate **2c** (0.20 g, 0.5 mmol) in DMF (12.5 mL) were added ethyl acrylate (5.0 g, 50 mmol), bis(triphenylphosphine)palladium(II) chloride (0.21 g, 0.30 mmol), and triethylamine (2.5 mL). The reaction mixture was stirred for 24 h at 130 °C and then cooled to rt. The mixture was poured into water and extracted with benzene (3 × 20 mL). The benzene extract was washed sequentially with 10% aqueous hydrochloric acid, water, and saturated aqueous sodium chloride and then dried over $MgSO_4$ and evaporated. Column chromatography (SiO_2, hexane) afforded 1,5-bis(β-carbethoxyethenyl)naphthalene **4b** as a yellow product (0.12 g, 75%).

1,5-Distyrylnaphthalene (5). To a solution of triflate **2c** (1.60 g, 4.0 mmol) in DMF (100 mL) were added styrene (5.20 g, 50 mmol), bis(triphenylphosphine)palladium(II) chloride (1.68 g, 2.4 mmol), and triethylamine (20 mL). The reaction mixture was stirred for 24 h at 130 °C and then cooled to rt. The mixture was poured into water and extracted with benzene (3 × 150 mL). The benzene extract was washed sequentially with 10% aqueous hydrochloric acid, water, and saturated aqueous sodium chloride and then dried over $MgSO_4$ and evaporated. Column chromatography (SiO_2, hexane) afforded 1,5-distyrylnaphthalene (**5**) as colorless crystals (0.59 g, 44%).

[2 + 2] Photocycloaddition of 1,5-Bis(β-carbethoxyethenyl)naphthalene. General Procedure. Olefin **4b** (32 mg, 0.1 mmol) was dissolved in dry benzene (100 mL) under a nitrogen atmosphere and was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter for 6 h. After evaporation of solvent, desired product **7b** was isolated by column chromatography (SiO_2, benzene). The yield was 15 mg (47%). Physical and analytical data are summarized in Tables II–IV and VI.

Synthesis of [4.4](2,6)Naphthalenophane. The mixture of naphthalenophanes **6g**, prepared by the photodimerization of olefin **3g** (20% yield), gave [4.4](2,6)naphthalenophane by means of a Birch reduction and a subsequent DDQ oxidation in 68% overall yield. The detailed reaction conditions were reported previously.[5] The structure of [4.4](2,6)naphthalenophane was determined by the comparison of the NMR spectrum with that of an authentic sample.[5]

Competitive Photoreaction of Divinylnaphthalenes. The 1:1 mixture of two different divinylnaphthalenes (0.1 mmol each) was dissolved in benzene-d_6 (1 mL) under a nitrogen atmosphere and was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter. The naphthalenophane formation was monitored by ^1H NMR spectroscopy. Results are summarized in Table V.

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Supplementary Material Available: Characterization data for **2a–h**, **3a-h**, **4a**, **4b**, and **5** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.