Effects of the Linkage Length and Substituents on the Photocycloaddition of Bis(vinylnaphthyl)alkanes toward Naphthalenophanes[1)]

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Many naphtalenophanes, including a dicarbomethoxy-substituted one, a di-4-pyridyl-substituted one, and a bis(trimethylsilyl)-substituted one, were synthesized by applying intramolecular [2+2] photocycloaddition of α, ω-bis(1-vinylnaphthyl) alkanes. The effect of the linkage and substituents at the α and/or β positions of the vinyl groups was investigated concerning this photocycloaddition. From the results of the investigation, the limitation and scope of the photocycloaddition toward naphthalenophanes has been established.

In addition to this preparative study, an anomalous transannular photoproduct, which was formed from *cis*, *exo*-1,2-ethano-*syn*-[2.3](1,4)naphthalenophane and analyzed by X-ray crystallography, was found to undergo thermal cycloreversion through diene and tetraene intermediates. The kinetics of this reversion were studied. Moreover, some obtained naphthalenophanes showed an interesting tendency to form 1 : 1 mixed crystals with small flat-shaped recrystallization solvents having donor substituents. This nature is also briefly reported.

Naphthalenophanes[2)] form a unique family in cyclophane chemistry, with respect to syntheses,[3,4)] photophysical properties,[5)] and reactivities.[6)] They have a variety of isomers due to the rather low symmetry of the naphthalene nucleus. This feature has attracted much interest in synthetic chemistry.[2)] Since naphthalenophanes have larger aromatic nuclei than do cyclophanes, the photophysical properties, such as excimer fluorescence emission, also attract much interest.[5)] Moreover, in an investigation of the intermolecular edge-to-face, or face-to-face, interactions between aromatic molecules, they could play an important role owing to their high solubility and accumulated electrostatic effects, though there has been only little work using the naphthalenophanes in this direction. Furthermore, their quite high photosensitivity can be pointed out as being one of the reasons for attracting so much attention; they usually undergo transannular [4+4] cyclization with syn configuration.[7)] A question, however, arises as to whether or not any other cyclization modes are possible in their skeletons.

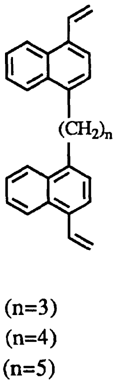
We recently proposed a systematic synthesis of the naphthalenophane family.[4)] By means of this method, several [2.*n*]-, [3.*n*]-, and [4.*n*]naphthalenophane skeletons can be readily constructed. Notably, this method gives structurally intriguing *syn*-naphthalenophanes exclusively. By applying this method,we have synthesized many new naphthalenophanes, have made the features of the method clear, have shown the limitation and scope, and have revealed new properties of the naphthalenophanes produced.

In this paper we would like to report on the effect of substituents at the α and/or β positions of the vinyl groups on the photocycloaddtion, new kinds of photocycloaddtion which occur in the naphthalenophane skeletons, a structural elucidation of the products by NMR spectroscopy and X-ray crystallography, and such properties of the products as the reactivity toward thermal cycloreversion and a tendency to form mixed crystals with recrystallization solvents.

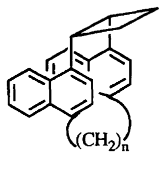
Results and Discussion

Intramolecular Photocycloaddition. The photocycloaddition of vinylnaphthalene derivatives has been reported in a few previous papers.[3,4,8)] These results are summarized in Table 1, together with newly obtained ones. The structures of all the naphthalenophanes were elucidated by NMR spectroscopy, including NOESY and COSY experiments. It was clarified that the naphthalenophane-forming step from **1** is affected by a conformation of the vinyl groups and the chain length of the vinylnaphthalene derivatives **1** (Chart 1).[4,8)]

Under irradiation, olefin **3a** with α-methyl substituents on the vinyl groups formed compound **6**[3)] instead of the normally expected naphthalenophane **7a**, although its regioisomer **5a** gave the expected **9** (see below). Yet, when tetramethylene was used as the linkage of monomer **3b**, the reaction to give a benzoequinene-



1a (n=3)
b (n=4)
c (n=5)



2a (n=3)
b (n=4)
c (n=5)

Chart 1.

Table 1. Preparation of Naphthalenophanes a)

Entry		Olefin				Conditions		Product b)	Yield	Remarks
		n	R	R_1	R_2	[Olefin] mM	Time h		%	
1	**1a**	3	H	H	H	10	9	**2a**	35	Ref. 8
2	**3a**	3	H	CH_3	H	8	24	**6**	21	Ref. 3
3	**3b**	4	H	CH_3	H	12	24	**7b**	6	Ref. 3
4	**4**	3	H	CH_3	H	6	24	**8**	1	Ref. 3
5	**5a**	3	H	CH_3	H	6	24	**9**	15	Ref. 3
6	**10a**	3	CH_3	H	Hc)	5	13	**11a**	18	Ref. 3
7	**10b**	4	CH_3	H	Hc)	10	36	**11b**	17	Ref. 3
8	**10c**	3	*i*-Pr	H	Hc)	10	12	**11c**	24	Ref. 3
9	**10e**	3	$SiMe_3$	H	Hc)	690	4	**11d**d)	4	This work
10	**10f**	3	γ-Py	H	Hc)	2	1	**11e**d)	23	This work
11	**10i**	3	COOMe	H	Hc)	5	18	**11f**	76	Ref. 3
12	**10j**	3	CN	H	H	2	24	**11g**,d) **12**d)	57e)	This work
13	**10k**	3	Ph	H	Hc)	4	12	**11h**	24	Ref. 3

a) Reaction conditions: in benzene under a N_2 atmosphere through a Pyrex filter with a 400-W high-pressure mercury lamp. See Refs. 3, 4, and 8 for the detailed procedure. b) Analytical data of the products are available in experimental. c) At photostationary state R_2 should be equal to R. d) NMR spectroscopic data serving the basis for the structural elucidation are listed in experimental. e) The exo, exo- and exo, endo-isomers (**11g** and **12**) were obtained in the 1 : 1 ratio.

type compound,9) like **6**, did not proceed at all.3) Alternatively, the normal [2+2] photocycloaddition took place to afford naphthalenophane **7b** in 6% yield. The structure of **7b** is of the endo configuration for the cyclobutane ring system. The same cyclization also occurred with olefin **4** (Chart 2).

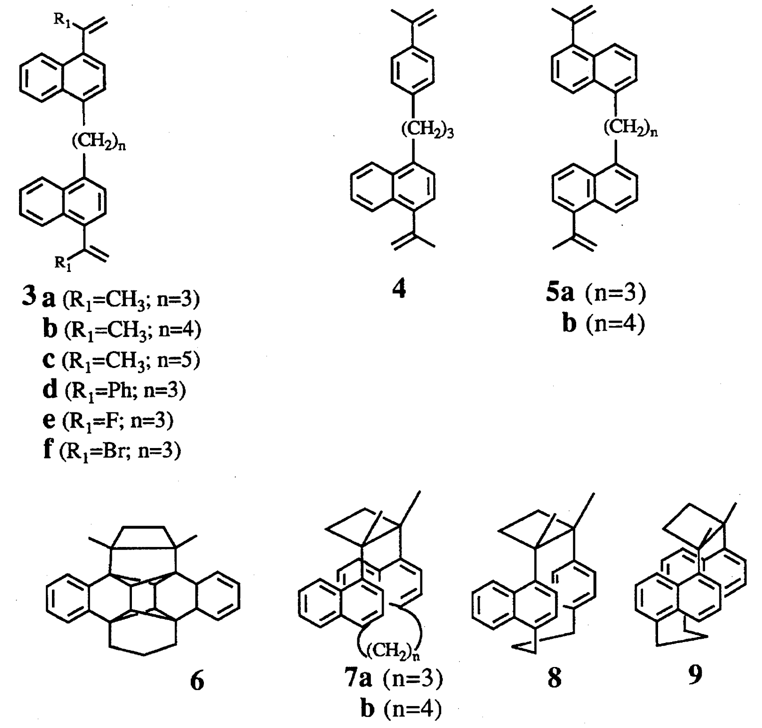
Accordingly, the selectivity is attributed to the conformation of isopropenyl group at the α-position of the naphthalene ring, which prefers the *exo*-methyl group and *endo*-olefinic methylene. When longer methylene chains were used, as seen in **3c** and **5b**, photoirradiation did not give any naphthalenophane derivatives. This seems to be due to a loss of the entropic advantage, although the chain length suitable for the synthesis of naphthalenophanes changes for different kinds of substrates.10) Eventually, it is notable that a change of only one methylene group, in the linkage dramatically changed the reaction course from the transannular type (**3a** to **6**), via the normal [2+2] cycloaddition (**3b** to **7b**), to an entirely different course from the intramolecular cycloaddition (**3c** to polymer).

Halo-substituted olefins behaved quite differently from others. α-Fluoro-**3e** and α-bromoolefin **3f** were prepared and irradiated, but did not give any desired naphthalenophanes. According to a ^{1}H NMR spectroscopic analysis of the reaction mixture, α-bromoolefin **3f** rearranged to the β-isomers and polymerized under further irradiation. This intriguing rearrangement has been already investigated by using styrene derivatives.11)

Many β-substituted olefins **10** were prepared and irradiated.3) Substituents at the vinyl β-position apparently exert a steric hindrance to this photocycloaddition. The introduction of two alkyl R, R_1- or R, R_2-substituents completely prevented the photocyclization from occurring, even if they were only small methyl groups. The R-substituent affected it less significantly than did the above cases; i.e., olefin **10c** with an isopropyl group gave naphthalenophane **11c** in 24% yield (Chart 3). The reaction, however, did not proceed with *t*-butyl groups at the β-positions. This is ultimately attributed to the extremely high strain loaded at the cyclobutane-ring formation step. On the other hand, trimethylsilyl groups did not affect the cyclization very severely, and actually gave the desired product in 4% yield. This is explained by the longer bond length of the Si–C bond (1.89 Å) than the C–C bond (1.54 Å) that reduces the steric hindrance occurring in the face-to-face arrangement of two vinylnaphthalene moieties. Phenyl12) and carbomethoxy groups13) for R substituents gave the desired naphthalenophanes, **11f** and **h**, in reasonably high yields, respectively.

Even if the reaction proceeds to afford *exo*, *exo* products **11**, the substituents mentioned above seem to be too large to produce any product with a substituent at the endo direction.14) Cyano-substituted olefin **10j** is unique in this respect. Photocyclization gave *exo*, *exo*-dicyanonaphthalenophane **11g** as well as *exo*, *endo*-one **12**, but not *endo*, *endo*-one (Chart 4). Most olefins are known to undergo *cis–trans* photoisomerization.15) Actually, *trans*, *trans*-olefin **10j**, which gave *exo*, *exo*-product **11g**, was isomerized to the *trans*, *cis*-one, which gave *exo*, *endo*-product **12**, and the *cis*, *cis*-one which could not cyclize, because the space surrounded by the cyclobutane ring and naphthalene β-hydrogens is too small to accommodate even the two relatively small CN groups.

A New Secondary Photorearrangement Prod-



3 a (R_1=CH_3; n=3)
b (R_1=CH_3; n=4)
c (R_1=CH_3; n=5)
d (R_1=Ph; n=3)
e (R_1=F; n=3)
f (R_1=Br; n=3)

4

5a (n=3)
b (n=4)

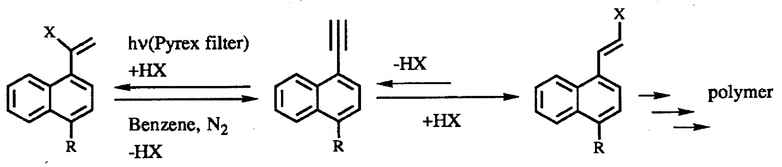
6

7a (n=3)
b (n=4)

8

9

Chart 2.



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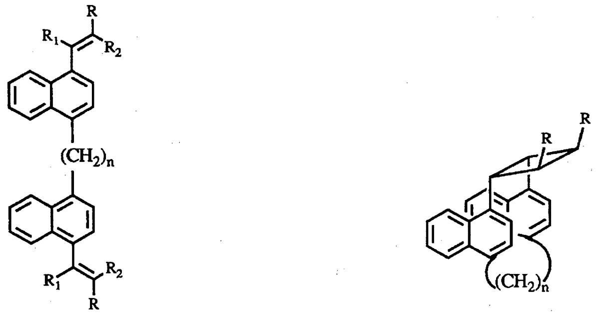


10a (R=CH_3; R_1, R_2=H; n=3)
b (R=CH_3; R_1, R_2=H; n=4)
c (R=i-Pr; R_1, R_2=H; n=3)
d (R=t-Bu; R_1, R_2=H; n=3)
e (R=$Si(CH_3)_3$; R_1, R_2=H; n=3)
f (R=γ-Py; R_1, R_2=H; n=3)
g(R=F; R_1, R_2=H; n=3)
h (R=Br; R_1, R_2=H; n=3)
i (R=$COOCH_3$; R_1, R_2=H; n=3)
j (R=CN; R_1, R_2=H; n=3)
k (R=Ph; R_1, R_2=H; n=3)
l (R, R_1=CH_3, R_2=H; n=3)
m (R, R_2=CH_3, R_1=H; n=3)

11a (R=CH_3; n=3)
b (R=CH_3; n=4)
c (R=i-Pr; n=3)
d (R=$Si(CH_3)_3$; n=3)
e (R=γ-Py; n=3)
f (R=$COOCH_3$; n=3)
g (R=CN; n=3)
h (R=Ph; n=3)

Chart 3.

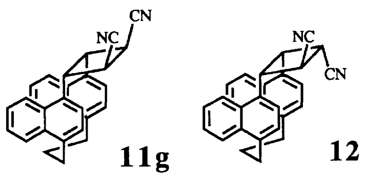


Chart 4.

uct. One new remarkable piece of evidence obtained after previous reports[3,4,8] is that further photoreaction of *cis*, *exo*-1,2-ethano-*syn*-[2.3]naphthalenophane **2a** gave photoproduct **13**, which underwent cycloreversion upon heating (see Charts 5 and 6). As far as we have examined, naphthalenophanes other than **2a** did not exhibit this kind of transannular reaction, even when they were treated under modified conditions of substrate concentration, irradiation time, the addition of a sensitizer, and so on. Although naphthalenophane **2a** reacted under direct irradiation in CH_2Cl_2 (but not in benzene) to afford cage compound **13**, *p*-dicyanobenzene as a photosensitizer accelerated this phototransannulation remarkably. Other photosensitisers such as acetophenone, benzophenone, and methyl 2-naphthyl ketone also activated the reaction to some extent, though not to the same extent as *p*-dicyanobenzene (see Experimental).

The ^{13}C NMR spectrum of **13** shows all 12 possible aromatic peaks, which indicate the lack of a symmetry plane for the simply expected transannular product **14** (see Experimental). An X-ray crystallographic analysis finally concluded the structure (see Fig. 1).

Compound **13** is believed to be formed from the three-fold consecutive $[2\pi+2\pi]$ cycloaddition product **14** through a $[2\sigma+2\sigma]$ photoreaction (C2–C5 and C6–C17). This kind of reaction with the participation of σ-bond cleavage at the benzyl position is known to exist for several substrates.[16] The rearrangement from **14** to **13** releases much strain energy, since the tricyclo[4.2.0.0^{2,5}]octane moiety contained in **14** is more strained by 52 kcal mol^{-1} than the tricyclo[3.2.1.0^{2,8}]octane moiety contained in **13**, according to an MM2 calculation (Chart 7).

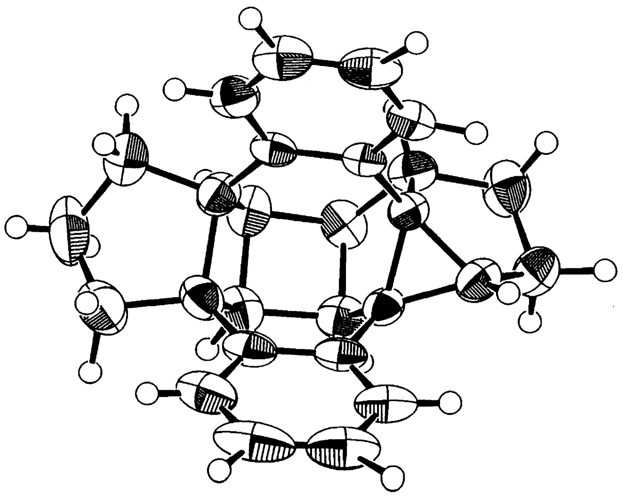


Fig. 1. ORTEP drawing of the structure of **13** (R=0.06).

According to an X-ray crystallographic analysis, photoproduct **13** has a cyclopropane ring, two cyclobutane rings, three cyclopentane rings, a boat-formed benzocyclohexene ring, a benzocycloheptane ring, and a tub-shaped dibenzocyclooctadiene ring. The analysis revealed the presence of two independent molecules (*a* and *b*) in a cell. A comparison between them and their remarkable features are given below.

Molecule *b* has one longer and two shorter bonds of the cyclopropane ring than does *a*, despite a moderate deviation from a normal cyclopropane C–C bond (1.532—1.504 Å vs. normal 1.510 Å[17]). Its trianglular shape is more deviated than that of molecule *a*. The dihedral angels between the cyclopropane and benzene ring planes are 95.3° (96.2°)[20] to 116.6° (120.7°),[18] so that the aromatic π-orbitals can conjugate with the Walsh-orbital of the cyclopropane C1–C6 bond.

Two cyclobutane rings are located in a bicyclo[2.2.0]hexane moiety. Although the inner cyclobutane ring has almost normal bond lengths (1.565—1.520 Å vs. normal 1.548 Å[19]), the outer one has remarkably elongated bonds, C9–C13 (1.635 and 1.627 Å for molecules *a* and *b*, respectively). The elongation of these benzyl carbon bonds seems to provide an explanation for the breaking of the C6–C17 and C5–C2 bonds of **14**: i.e., these bonds in **14** would become considerably long to break to release the strain accumulated.

The cage compound **13** could be thermolyzed to olefin **1a**, naphthalenophane **2a**, and polymeric material. The thermolysis was investigated in order to clarify the mechanism. During the reaction at 160°C, two intermediates were observed by ^{1}H NMR spectroscopy, the spectra of which are shown in Fig. 2. Three peaks (a triplet at $\delta=4.78$, a doublet at $\delta=5.25$, and a multiplet at $\delta=5.51$ which are assigned to the intermediates) increased at the beginning of the reaction and then decreased. Besides, two double doublets appearing at $\delta=5.42$ and 5.74 are assigned to the vinyl groups of **1a**, and increased along the time course; a multiplet appearing at $\delta=5.04$, assigned to naphthalenophane **2a**, also increased.

One of the intermediates **15** was isolated by preparative HPLC (reversed phase C-18, MeOH), showing two former peaks at $\delta=4.78$ and 5.25. In order to assign the intermediates, compound **13**-d_2 was prepared and then thermolyzed. During the reaction only a double doublet peak at $\delta=5.25$ was observed, as shown in Fig. 2. Because the triplet at $\delta=4.78$ disappeared, intermediate **15** is assigned to the depicted compound (see Fig. 2). Another intermediate showing a multiplet is assigned to **16**. Other reaction products did not show any sharp signals in the reaction mixture according to ^{1}H NMR spectroscopy. A TLC analysis of the thermolysis mixture clearly indicated the presence of polymeric mate-

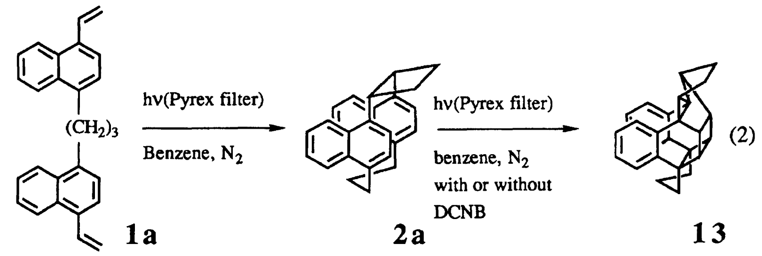


Chart 5.

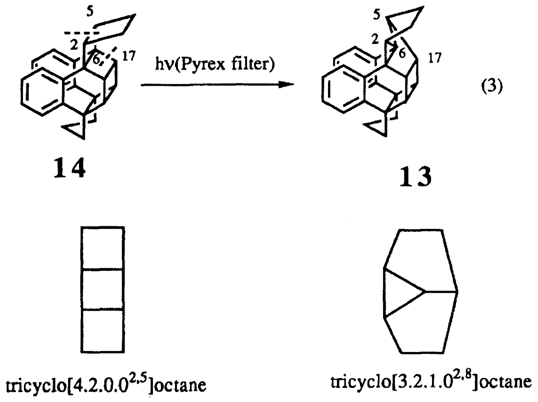


Chart 6.

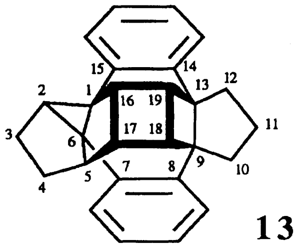


Chart 7.

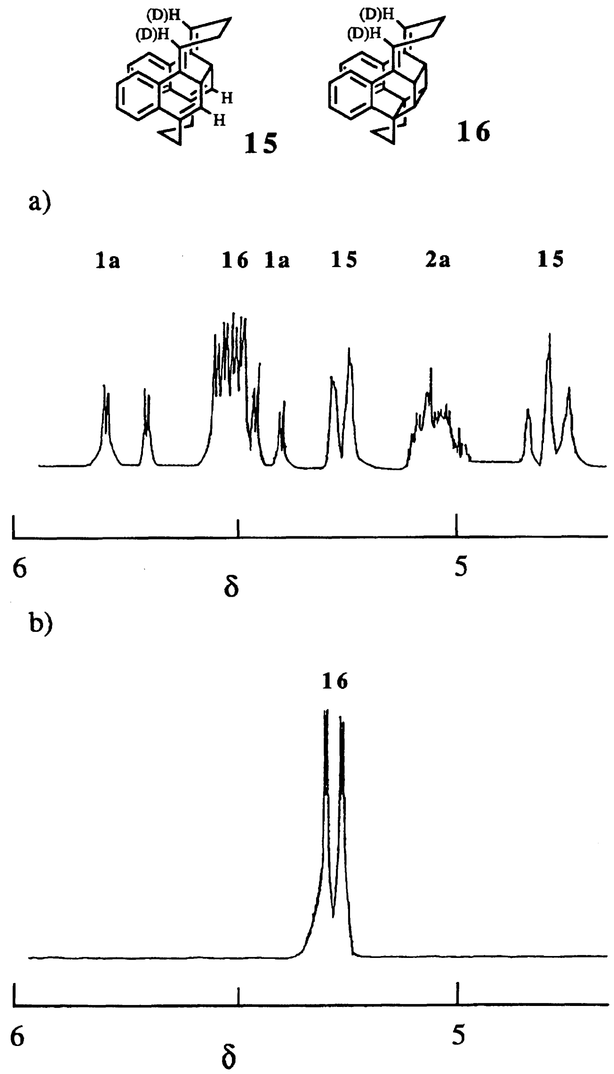


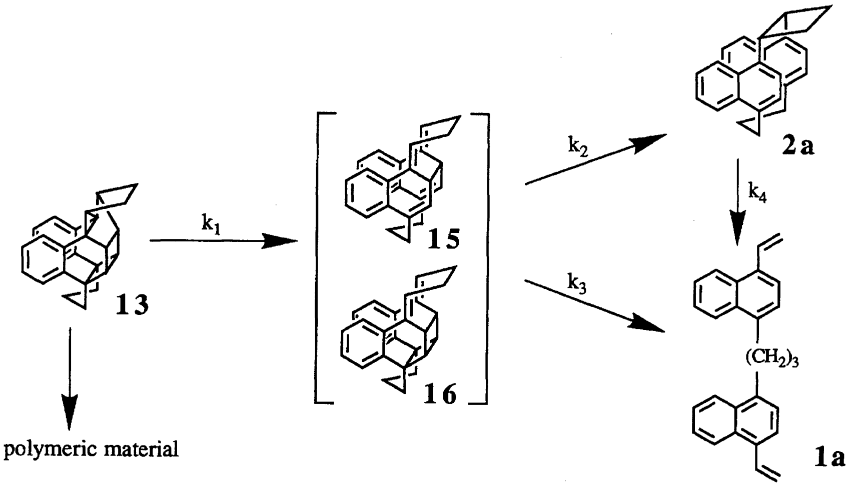
Fig. 2. ^{1}H NMR spectra of the thermal reaction mixtures from cage compound **13** and its deuterated one **13**-d_2; a) from **13** and b) from **13**-d_2.

rials. Hence, a mechanism for the reaction is proposed, as shown in Scheme 1. Since the intermediates were formed and consumed at almost the same rates, they were both treated together in this kinetics. Rate constants k_1 to k_4 were calculated by a computer simulation, as shown in Fig. 3, and summarized in Table 2. The thermodynamic parameters are listed in Table 3.

Tendency to Make 1 : 1 Mixed Crystals with Solvents. An X-ray crystallographic analysis of **2a** revealed an interesting feature, as shown in Fig. 4, a compound made of 1 : 1 mixed crystals with recrystallization solvents. Unfortunately, the transparent needle mixed crystals were not stable and became white within a short period due to efflorescence.

The tendency for some naphthalenophanes to make mixed crystals was examined using several solvents, and is summarized in Table 4. The composition of the naphthalenophanes and solvents was always 1 : 1. Naphthalenophane **2a** could make such crystals with benzene, toluene, aniline, pyridine, pyrrole, furan, and thiophene, but not with ethylbenzene, *o*-, *m*-, and *p*-xylene, halo-benzenes, nitrobenzene, cyclohexane, and naphthalene (in $CDCl_3$). The tendency to form mixed crystals with benzene decreased with the length of the naphthalenophane tether from trimethylene (**2a**) to pentamethylene (**2c**), which causes a deformation from the parallel arrangement of the naphthalene rings in the molecule.$^{20)}$ Dimethyl substitution at the cyclobutane ring (**11a**) did not drastically affect the tendency.

Hence, mixed crystals can be easily formed when



Scheme 1. Thermal Reaction of Cage Compound **13**.

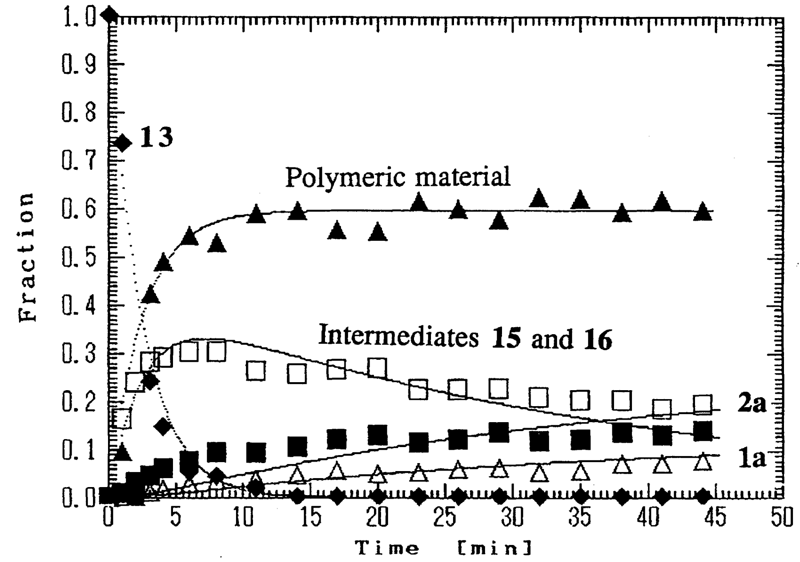


Fig. 3. Time course of the thermal reaction of cage compound **13** at 175°C.

Table 2. Kinetic Data of the Thermolysis of Cage Compound **13** [a)]

	Rate constant/$\times 10^{-4}$s^{-1}				
	160°C	170°C	175°C	180°C	190°C
k_1	5.1	13.7	27.0	29.7	31.0
k_2	0.883	2.67	3.00	5.50	9.33
k_3	0.427	0.833	1.50	3.00	5.00
k_4	—	—	—	0.446[b)]	—

a) The simulation gave ±10% accuracy. b) Measured independently.

Table 3. Thermodynamic Parameters of Thermolysis of Cage Compound **13**

	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/e.u.	$\Delta G^{\neq}_{160^\circ\mathrm{C}}$/kcal mol^{-1}
k_1	33.5±0.3	2.98±0.02	32.3±0.3
k_2	31.0±0.2	−6.38±0.05	33.8±0.3
k_3	34.3±0.5	−0.516±0.008	34.5±0.5

naphthalenophanes have a rectangular shape enclosed by naphthalene rings and flat-shaped small compounds with an electron-donating group are used as the solvent. The electron-donating nature of the solvent seems to facilitate the tendency to make such crystals, because of the fact that two solvents having almost the same sized substituents, toluene and chlorobenzene, behaved entirely differently. As far as the **2a**-benzene crystal structure was concerned, however, the included benzene was not properly arranged[21)] to interact electrostatically with the naphthalene rings in a face-to-face fashion, or in a face-to-edge one that might cause an attractive interaction.[22)] At this moment the electrostatic attractive force between a naphthalenophane and a solvent molecule appears to work for some preorganization to produce the crystal lattice.

Conclusion

Many substituted naphthalenophanes were synthesized. The details concerning the method and its limita-

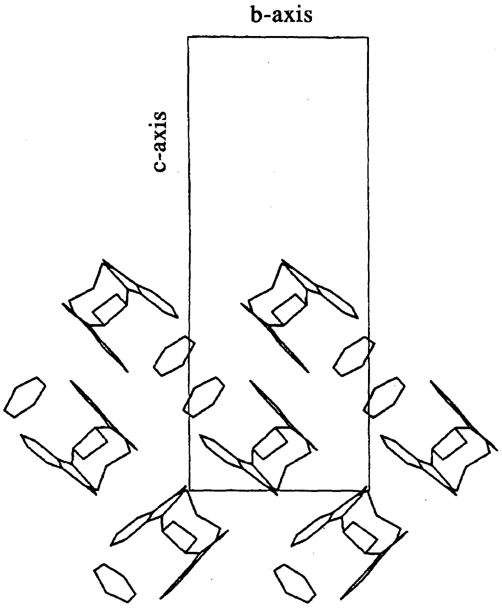


Fig. 4. *a*-Axis projection of naphthalenophane **2a**-benzene crystal structure (R=0.2).

Table 4. Mixed Crystals of Naphthalenophanes with Some Solvents $^{a)}$

Naphthalenophane	Solvent$^{b)}$	Remarks
2a(R=H; n=3)	Benzene	Needle, transparent
	Toluene	Needle, transparent
	Aniline	Needle, transparent
	Pyridine	Needle, transparent
	Furan	Plate, transparent
	Thiophene	Needle, transparent
	Pyrrole	Needle, transparent
2b(R=H; n=4)	Benzene	Needle, transparent
2c(R=H; n=5)	Benzene$^{c)}$	Needle, transparent
11a(R=CH_3; n=3)	Benzene	Needle, transparent

a) Recrystallization conditions: solvent, 2.0 ml; naphthalenophane, 50 mg; stand at r.t. in a capped vail. b) The composition of naphthalenophane and solvent in crystals was determined by ^{1}H NMR spectroscopy after dissolved in $CDCl_3$ and was found always 1 : 1 within an experimental error. c) Only the pure crystal of **2c** was obtained.

tion and scope were clarified: The effects of substituents at the α and/or β positions of the vinyl groups were investigated concerning this photocycloaddition. When a methyl group was substituted at the α position of the vinyl group, one methylene group difference at the linkage dramatically changed the reaction course. Substituents at vinyl β position exerted an apparent steric hindrance on the reaction. Halo-substituted olefins underwent a rearrangement through the formation of an acetylene moiety under irradiation, and finally polymerized. Photoproduct **13** of naphthalenophane **2a** was analyzed by X-ray crystallography; **13** underwent thermal cycloreversion through intermediates like **15** and **16**. The kinetics of the reaction were examined. Some naphthalenophanes showed a tendency to form 1 : 1 mixed crystals with small flat-shaped recrystallization solvents having donor substituents.

Experimental

General The NMR spectra were recorded on a Varian Gemini-200 FT NMR spectrometer. X-Ray crystallographic measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu $K\alpha$ radiation and a 12 kW rotating-anode generator. Mass spectra were taken on a JEOL JMS-DX303 mass spectrometer. An HPLC analysis was performed using a Shimadzu LC-6A pump, and an LC-6A UV detector, and an RC4A data processor. The melting points are not corrected. The MM2 program was cordially provided by Prof. Eiji Osawa of Toyohashi University of Technology.

Materials. Benzene was purified by distillation over Na after prolonged reflux under a N_2 atmosphere. Other commercially available reagents of highest grade were used without further purification. The starting olefins were prepared by the reported methods with some minor modifications.[3,4] Deuterated olefin **1a**-d_2 was prepared form 1,3-bis[4-(1-hydroxyethyl-1-d)-1-naphthyl]propane made by an $LiAlD_4$ reduction of the corresponding ketone.

Photocycloaddition of Olefin (General Method). Olefin **1a** (1.16 g, 3.33 mmol), dissolved in dry benzene (300 mL), was irradiated through a Pyrex filter with a 400-W high-pressure mercury lamp under a N_2 atmosphere for 9 h. After evaporation of the solvent, the crude reaction product was treated with a 1 M BH_3–THF solution[8] (2 mL) and stirred for 15 h. Evaporation in vacuo left a residue which, on column chromatography (SiO_2, hexane), afforded naphthalenophane **2a** in 35% yield (0.406 g).

The melting points, analytical, and spectroscopic data of new naphthalenophanes obtained this work are as follows:

11d, mp 186—187°C; MS (M$^{\cdot+}$, m/z) Calcd for $C_{33}H_{40}Si_2$: M, 492.2670. Found: m/z 492.2668; ^{1}H NMR (intensity, multiplicity, coupling constant J in Hz) δ=7.52 (2H, m), 7.39 (2H, m), 6.85 (8H, m), 4.87 (2H, d, J=7.2 Hz), 3.59 (2H, m), 2.70 (3H, m), 2.69 (2H, d, J=7.2 Hz), 2.20 (1H, m) and 0.26 (9H, s).

11e, mp 171—173°C; MS (M$^{\cdot+}$, m/z) Calcd for $C_{37}H_{30}N_2$: M, 502.2411. Found: m/z 502.2409; ^{1}H NMR (intensity, multiplicity, coupling constant J in Hz) δ=8.49 (2H, m), 7.56 (2H, m), 7.46 (2H, m), 7.23 (2H, m), 6.90 (8H, m), 5.23 (2H, d, J=6.0 Hz), 4.74 (2H, d, J=6.0 Hz), 3.62 (2H, m), 2.75 (3H, m), and 2.27 (1H, m).

11g, mp 247—248°C; MS (M$^{\cdot+}$, m/z) Calcd for $C_{29}H_{22}N_2$: M, 398.1785. Found: m/z 398.1783; ^{1}H NMR (intensity, multiplicity, coupling constant J in Hz), δ=7.44 (4H, m), 6.95 (4H, m), 6.85 (2H, d, J=7.4 Hz), 6.51 (2H, d, J=7.4 Hz), 5.46 (2H, d, J=6.0 Hz), 4.21 (2H, d, J=6.0 Hz), 3.63 (2H, m), 2.72 (3H, m), and 2.26 (1H, m).

12, mp 271—273°C; MS (M$^{\cdot+}$, m/z) Calcd for $C_{29}H_{22}N_2$: M, 398.1785. Found: m/z 398.1783; ^{1}H NMR (intensity, multiplicity, coupling J in Hz) δ=7.39 (4H, m), 7.04—6.67 (8H, m), 5.53 (2H, m), 5.46 (1H, m), 5.36 (1H, m), 3.63 (2H, m), 2.74 (3H, m), and 2.27 (1H, m).

Photoreaction of Naphthalenophane 2a. Naphthalenophane **2a** (1.16 g, 3.33 mmol) and p-dicyanobenzene (42.7 mg, 0.33 mmol, 10 mol%) were irradiated in

CH_2Cl_2 (300 ml) at r.t. through a Pyrex filter by a 400-W high-pressure mercury lamp under an N_2 atmosphere for 12 h. After the same workup procedure as mentioned above, photoadduct **13** was obtained in 81% yield. When acetophenone, benzophenone, and methyl 2-naphthyl ketone were used, the yields of **13** were 74, 60, and 57%, respectively. Without any sensitizer, the yield decreased to 13%. Mp 161—162°C; MS ($M^{\cdot+}$, m/z) Calcd for $C_{27}H_{24}$: M, 348.1878. Found: m/z=318.1876; ^1H NMR (intensity, multiplicity, coupling constant J in Hz) δ=7.31 (1H, m), 7.15 (1H, m), 7.05 (1H, m), 7.00—6.86 (5H, m), 3.20 (1H, m), 3.12 (1H, d, J=6.7 Hz), 2.85 (1H, m), 2.61 (3H, m), 2.48—2.10 (4H, m), 2.08 (2H, m), 1.74 (3H, m), and 1.31 (1H, dd, J=12,0 & 7.8 Hz). ^{13}C NMR (intensity) δ=138.1 (1C), 137.9 (1C), 137.1 (1C), 135.7 (1C), 122.8 (1C), 122.3 (2C), 122.0 (1C), 121.9 (1C), 121.8 (1C), 121.5 (1C), 119.8 (1C), 57.2 (1C), 53.5 (1C), 53.1 (1C), 51.7 (1C), 48.1 (1C), 43.3 (1C), 40.9 (1C), 38.1 (1C), 36.4 (1C), 35.6 (1C), 31.7 (1C), 31.2 (1C), 28.2 (1C). 21.1 (1C), and 19.9 (1C).

Thermal Cycloreversion of Cage Compound 13. Compound **13** (30.0 mg) and trimethylphenylsilane (2.0 mg) as an internal standard were set in an NMR sample tube and dissolved in nitrobenzene-d_5 (0.5 ml). After three freeze-and-thaw degassing cycles, the sample tube was sealed and set in a probe heated at the prescribed temperatures. After the sample reached the temperature (ca. 5 min), data were taken up to 95% conversion of compound **13**.

X-Ray Crystallographic Analysis of Cage Compound 13 and 2a.[23] **Compound 13:** $C_{27}H_{24}$, M=348.492. The crystal belongs to the monoclinic system, space group $P2_1/a$, Z=8. Cell parameters: a=18.514 (4), b=12.319 (3), c=18.168 (4) Å, β=119.56 (1), V=3604 (1) Å^3, d_c=1.284 g cm^{-3}, $\lambda(CuK\alpha)$=1.54178 Å. Diffractometric intensity data were obtained from a crystal of dimensions 0.3×0.3×0.1 mm. From 5849 unique reflections collected by the ω–2θ scan-technique up to 2θ=120.2°, only 5651 reflections with $F_o \geq 3\sigma(F_o)$ were retained in refinement calculations. The structures were solved by direct methods using TEXSAN, and then refined by least-squares while minimizing the function $\Sigma w(\Delta F)^2$. Most of the hydrogen atoms were located on difference Fourier maps. The final conventional R factor was 0.062.

Compound 2a: $C_{27}H_{24}\cdot$ benzene, M=426.607. The crystal belongs to the orthorhombic mmm, space group $P2_12_12_1$, Z=4. Cell parameters: a=10.499 (1), b=23.823 (2), c=9.439 (0) Å, V=2361 (0) Å^3, $\lambda(CuK_\alpha)$=1.54178 Å. Diffractometric intensity data were obtained from a crystal of dimensions 0.3×0.2×0.2 mm. From the unique reflections collected by the ω–2θ scan-technique up to 2θ=126°, only 1876 reflections with $F_o \geq 3\sigma(F_o)$ were retained in refinement calculations. The structures were solved by direct methods using MULTAN 80, and then refined by least-squares while minimizing the function $\Sigma w(\Delta F)^2$. The final conventional R factor was 0.2, and was not refined because of the unstable crystal.

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