# Intramolecular [2+2] Photocycloaddition. 5.[1] Synthetic Methods toward [2.*n*]-, [3.*n*]-, and [4.*n*]Naphthalenophane Skeletons by Using α,ω-Bis(vinylnaphthyl)alkanes

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[2+2] Photocycloaddition, cationic cyclocodimerization, and reductive ring enlargement were developed for the syntheses of [2.*n*]-, [3.*n*]-, and [4.*n*]naphthalenophanes, respectively, from α,ω-bis(vinylnaphthyl)-alkanes as a single starting material. Using the exclusive syn selectivity of the former two methods, the room required for the intraannular naphthalene-ring rotation in the ring system is determined.

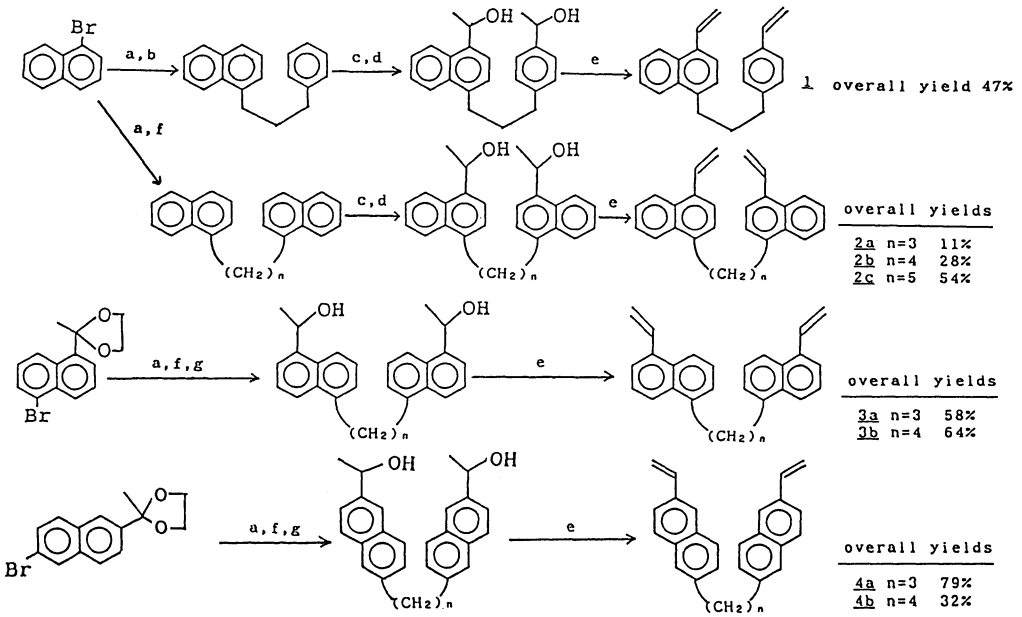
Several naphthalenophanes were already made by 1,6-Hoffman degradation,[2] by solvolysis of appropriate tosylate,[3] by malonate synthesis[4] and tosmic synthesis,[5] and by using dithia intermediates as the most general precursor.[6] Until now *syn*- and *anti*-[2.2](1,4)naphthalenophane,[2] chiral and achiral [2.2](2,6)napthalenophane,[6] [2.2](2,7)naphthalenophane,[7] [2.2](2,6)(2,7)naphthalenophane,[8] [2.2]paracyclo-(1,4)- and (2,6)naphthalenophane,[9] *syn*- and *anti*-[3.3](1,4)naphthalenophane,[4] and chiral and achiral [3.3](2,6)naphthalenophane[10] were reported.

We developed some new methods toward these structurally, physicochemically interesting naphthalenophanes.[11] Here in this paper, we report a photochemical route toward [2.*n*]naphthalenophanes from vinylnaphthalene derivatives and their Birch reduction to [4.*n*] ones together with some application of cationic cyclocodimerization[12] to [3.*n*] skeletons. Moreover we determined the room required for the naphthalene ring rotation after Birch reduction of the conformationally unstable *syn*-naphthalenophane derivatives.

## Results

**Preparation of Vinylnaphthalenes.** Synthetic methods of starting materials are depicted in Chart 1. The standard conditions were already reported for several vinylarene derivatives.[13]

Only the preparation of 2-acetyl-6-bromonaphthalene did not record satisfactory yields. For a large scale preparation, the material should be obtained by other routes than this method which is based on the equilibrium attained in the Friedel-Crafts acylation of 2-bromonaphthalene.[14]




a) Mg/THF. b) Br(CH2)3Ph, CuBr-HMPA. c) CH3COCl, AlCl3/CH2ClCH2Cl. d) LiAlH4/ether. e) KHSO4/DMSO. f) Br(CH2)nBr, CuBr-HMPA. g) HCl/DOX-H2O.

Chart 1. Preparation of vinylnaphthalenes.

**Synthesis of [2.*n*]Naphthalenophane Derivatives.** Intramolecular [2+2] photocycloaddition of vinylnaphthalene derivatives **1—4** successfully gave corresponding naphthalenophanes **5—8** as reported briefly.[11] By this method *syn*-[2.*n*]paracyclo(1,4)-, *syn*-[2.*n*](1,4)-, *syn*-[2.*n*](1,5)-, and [2.*n*](2,6)-naphthalenophanes were prepared. The reaction gives exclusively syn isomer, because the vinyl group has only exo conformation (conformational rigidity of vinyl group[15]) and never attains an endo, exo-divinyl combination for the formation of anti isomer. This selectivity is quite important, because previously reported synthetic methods listed above generally give conformationally stable *anti*-naphthalenophanes exclusively.

Reactions together with their yields are shown in Chart 2. Physical, analytical, and spectroscopic data of products are listed in Tables 1 and 2.

The reaction mixture of olefin **4** showed two HPLC peaks (Cosmosil-C18, MeOH) in the range where naphthalenophanes of this sort should be eluted. These two compounds were isolated from a small portion of the mixture by HPLC for the structural determination, and the major portion was treated by Birch reduction as described below.

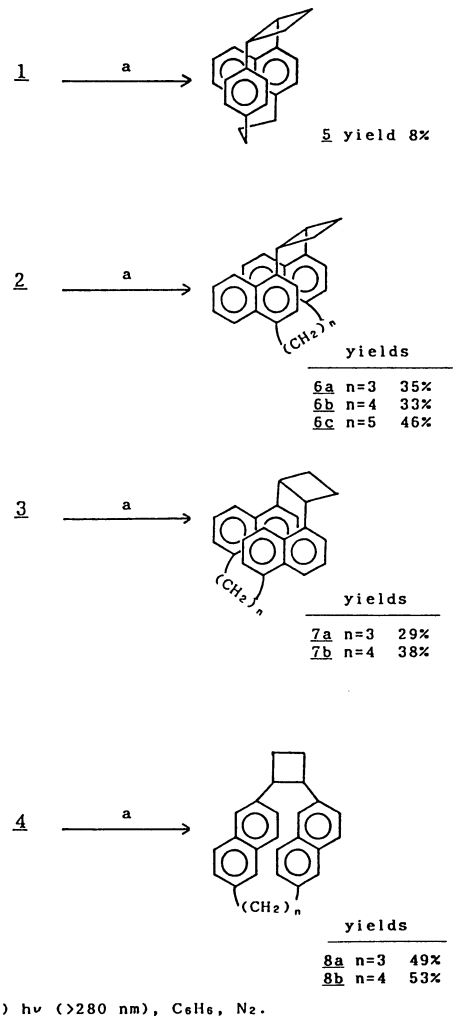



Chart 2. [2+2] Photocycloaddition toward [2.*n*]-naphthalenophanes.

Table 1. Physical and Analytical Data of Novel Naphthalenophanes

| Compd[a] | MP $\theta_m$/°C | MS ($M^+$, $m/z$) calcd (found) | Found (%) C | Found (%) H | Calcd (%) C | Calcd (%) H |
|---|---|---|---|---|---|---|
| **5** | 141—142 | 298.1723(298.1713) | 92.63 | 7.36 | 92.57 | 7.43 |
| **6a** | 219—221 | 348.1879(348.1881) | 93.21 | 6.87 | 93.06 | 6.94 |
| **6b** | 220—222 | 362.2036(362.2041) | 92.47 | 7.40 | 92.77 | 7.23 |
| **6c** | 233—234 | 376.2192(376.2186) | 92.42 | 7.44 | 92.50 | 7.50 |
| **7a** | 234—235 | 348.1879(348.1868) | 92.89 | 7.02 | 93.06 | 6.94 |
| **7b** | 233—234 | 362.2036(362.2028) | 92.48 | 7.28 | 92.77 | 7.23 |
| **15a**[b] | 179—181 | 466.2660(466.2668) | | | | |
| **15b**[c] | 200—201 | 480.2819(480.2823) | | | | |
| **16**[d] | 228—229 | 466.2660(466.2660) | | | | |
| **17**[e] | 76—78 | 466.2660(466.2652) | | | | |
| **18** | —[f] | 300.1879(300.1876) | 91.76 | 8.07 | 91.95 | 8.05 |
| **19a** | 208—209 | 350.2036(350.2029) | 92.51 | 7.57 | 92.52 | 7.48 |
| **19b** | 258—259 | 364.2192(364.2193) | 92.13 | 7.78 | 92.26 | 7.74 |
| **19c** | 110—111 | 378.2349(378.2343) | 91.83 | 7.91 | 92.01 | 7.99 |
| **20a** | 228—230 | 350.2036(350.2035) | | | | |
| **20b** | 294—295 | 364.2192(364.2194) | 92.22 | 8.04 | 92.26 | 7.74 |
| **21a** | 230—232 | | 92.27 | 7.63 | 92.52 | 7.48 |
| **21b**[g] | 225—228 | 364.2192(364.2194) | | | | |
| **22a** | 235—236 | | 92.38 | 7.58 | 92.52 | 7.48 |

a) Melting points of new olefins are as follows: **2b**, 139—140; **2c**, 103—104; **3a**, 79—80; **3b**, 104—105; **4a**, 174—175 ; **4b**, 167—168. b) IR absorption of three substituted olefin appears at 813 $cm^{-1}$. c) IR absorption at 813 $cm^{-1}$. d) IR absorption at 817 $cm^{-1}$. e) IR absorption at 815 $cm^{-1}$. f) Not determined. g) This is a conformationally fluxional compound, so that it contains **22b** as a conformational isomer (see text for details).

**Synthesis of [3.*n*]Naphthalenophane Derivatives.** One of the synthetic methods for [3.*n*]naphthalenophanes is the cationic cyclocodimerization, although the structures of naphthalenophanes produced are intricate with two substituents at one of their linkages.[12,15] The detailed feature of the reaction has been already discussed with some naphthalenophane derivatives.[15] In this work this cationic cyclization was employed for the synthesis of [3.*n*](1,5)- and [3.*n*](2,6)-skeletons.

Because of the conformational rigidity of the α-vinyl group, only one isomer of 1-methyl-3-(β-methylstyryl)[3.3](1,5)naphthalenophane **15a** was obtained in a reasonable yield from olefin **3a**. The structure was determined by NOESY spectroscopy. A large NOE enhancement (12%) is observed between a peri-hydrogen and allylic hydrogen (H-3).[16] The results clearly indicate that naphthalenophane **15a** is an exo, cis-isomer (See Ref. 16 for the definition of exo, endo-configuration). Syn conformation of **15a** is assigned unequivocally by comparison of the chemical shifts of aromatic proton resonances with those of [3.3](1,4)naphthalenophane derivatives. Accordingly the structure of **15a** is determined as depicted in Chart 3. Since an anti-oriented cation of the reaction

Table 2. $^1$H NMR Spectroscopic Data of Novel Vinylarenes and Naphthalenophanes[a)]

| Compd | Chemical shift $\delta$ (intensity, multiplicity, $J$ in Hz) |
|---|---|
| **2b** | 8.14 (2H, m), 8.05 (2H, m), 7.54—7.37 (8H, m), 7.28 (2H, d, 7.6), 5.74 (2H, dd, 17.2 and 1.6), 5.42 (2H, dd, 11.0 and 1.6), 3.10 (4H, m) , 1.88 (4H, m). |
| **2c** | 8.13 (2H, m), 8.04 (2H, m), 7.52—7.44 (6H, m), 7.46 (2H, dd, 17.2 and 10.8), 7.26 (2H, d, 7.6), 5.74 (2H, dd, 17.2 and 1.7), 5.42 (2H, dd, 10.8 and 1.7), 3.04 (4H, t, 7.7), 1.80 (4H, quint, 7.7), 1.54 (2H, m). |
| **3a** | 7.99 (2H, d, 7.9), 7.91 (2H, d, 7.9), 7.64—7.30 (10H, m), 5.76 (2H, dd, 17.9 and 1.2), 5.46 (2H, dd, 10.7 and 1.2), 3.20 (4H, t, 7.1), 2.25 (2H, quint, 7.1). |
| **3b** | 8.04 (2H, dd, 8.4 and 1.5), 8.03 (2H, dd, 8.4 and 1.5), 7.68—7.31 (10H, m), 5.80 (2H, dd, 17.2 and 1.6), 5.50 (2H, dd, 10.8 and 1.6), 3.15 (4H, m) , 1.93 (4H, m). |
| **4a** | 7.74 (2H, bd, 10.1), 7.72 (2H, bd, 8.4), 7.71 (2H, bs), 7.62 (2H, dd, 10.1 and 1.7), 7.57 (2H, bs), 7.32 (2H, dd, 8.4 and 1.9), 6.87 (2H, dd, 17.5 and 10.8), 5.84 (2H, dd, 17.5 and 1.1), 5.30 (2H, dd, 10.8 and 1.1), 2.83 (4H, t, 7.4), 2.12 (2H, quint, 7.4). |
| **4b** | 7.75—7.60 (6H, m), 7.59 (2H, dd, 7.8 and 1.6), 7.55 (2H, bs), 7.29 (2H, dd, 8.4 and 1.8), 6.87 (2H, dd, 16.8 and 10.8), 5.84 (2H, dd, 16.8 and 0.8), 5.30 (2H, dd, 10.8 and 0.8), 2.80 (4H, m), 1.78 (4H, m). |
| **5** | 7.76 (1H, m), 7.68 (1H, m), 7.35 (2H, m), 6.80 (1H, d, 7.3), 6.68 (1H, dd, 7.8 and 1.7), 6.64 (1H, d, 7.3), 6.60 (1H, dd, 7.8 and 1.7), 5.73 (1H, dd, 8.0 and 1.7), 5.30 (1H, dd, 8.0 and 1.7), 4.93 (1H, m), 3.88 (1H, m), 3.54 (1H, m), 2.73 (4H, m), 2.50—2.20 (4H, m), 2.06 (1H, m). |
| **6a** | 7.45 (2H, m), 7.38 (2H, m), 6.82 (4H, m), 6.74 (4H, t, 6.6), 5.04 (2H, m), 3.59 (2H, dd, 13.6 and 3.8), 2.67 (7H, m), 2.15 (1H, m). |
| **6b** | 7.67 (2H, m), 7.41 (2H, m), 6.99 (2H, ABq, 7.4), 6.91 (4H, m), 6.83 (2H, ABq, 7.4), 5.09 (2H, m), 3.07 (2H, m), 2.76 (4H, m), 2.34 (2H, m), 1.61 (4H, bs). |
| **6c** | 7.86 (2H, dd, 7.4 and 2.4), 7.44 (2H, dd, 7.4 and 2.2), 7.13 (2H, d, 7.4), 7.02 (4H, m), 6.85 (2H, d, 7.4), 5.10 (2H, m), 3.27 (2H, dt, 13.6 and 4.2), 2.79 (4H, m), 2.33 (2H, td, 12.8 and 4.2), 1.62 (2H, m), 0.96 (2H, m), 0.55 (2H, m). |
| **7a** | 7.41 (2H, d, 7.9), 7.33 (2H, d, 8.4), 6.89 (2H, t, 7.9), 6.82 (4H, m), 6.68 (2H, d, 6.8), 5.03 (2H, m), 3.59 (2H, m), 2.74 (7H, m), 2.06 (1H, m). |
| **7b** | 7.55 (2H, bd, 8.4), 7.33 (2H, bd, 8.0), 6.90 (6H, m), 6.68 (2H, bd, 7.2), 5.06 (2H, m), 3.06 (2H, m), 2.75 (4H, m), 2.30 (2H, m), 1.53 (4H, bs). |
| **15a** | 6.68—7.70 (17H, m), 6.16 (1H, d, 8.8), 4.60 (1H, m), 3.74 (1H, m), 3.58 (2H, m), 2.88 (3H, m), 2.16—2.57 (3H, m), 2.14 (3H, s), 1.38 (3H, d, 7.4). |
| **15b** | 7.84 (1H, bd, 8.8), 7.74 (1H, bd, 8.8), 7.39—7.18 (8H, m), 7.11 (1H, dd, 7.2 and 1.1), 6.94 (4H, m), 6.82 (1H, bd, 7.1), 6.73 (1H, bd, 7.1), 6.14 (1H, dd, 8.3 and 1.3), 4.69 (1H, ddd, 11.2, 18.8, and 2.9), 3.87 (1H, m), 3.12 (2H, m), 2.67 (1H, m), 2.39 (3H, m), 2.13 (3H, d, 1.4), 1.81 (4H, m), 1.37 (3H, d, 7.0). |
| **16** | 7.13—7.37 (9H, m), 7.08 (4H, bs), 6.88 (4H, m), 6.02 (1H, dd, 9.1 and 1.8), 3.79 (1H, ddd, 11.5, 9.1, and 2.8), 3.04 (1H, m), 2.95 (2H, m), 2.83 (2H, m), 2.22 (3H, m), 2.13 (3H, d, 1.8), 1.95 (1H, m), 1.31 (3H, d, 7.0). |
| **17** | 7.01—7.38 (13H, m), 6.85 (1H, bs), 6.79 (1H, bs), 6.73 (1H, bs), 6.66 (1H, bs), 5.94 (1H, dd, 9.4 and 1.5), 3.73 (1H, ddd, 13.2, 9.4, and 4.0), 2.81 (5H, m), 2.24 (3H, m), 2.15 (3H, d, 1.5), 1.98 (1H, m), 1.33 (3H, d, 7.2). |
| **18** | 8.04 (2H, m), 7.83 (2H, m), 7.44 (2H, m), 6.79 (2H, bd, 8.2), 6.71 (2H, d, 7.2), 6.62 (2H, bd, 8.2), 6.57 (2H, d, 7.2), 5.82 (2H, bs), 3.59 (1H, m), 3.25 (1H, m), 2.78 (2H, m), 2.58 (2H, m), 2.39 (2H, m), 2.18 (2H, m), 1.95 (2H, m), 1.40 (2H, m). |
| **19a** | 8.13 (2H, m), 7.85 (2H, m), 7.49 (4H, m), 6.02 (2H, d, 7.2), 5.88 (2H, d, 7.2), 3.55 (2H, m), 3.31 (2H, m), 2.78 (2H, m), 2.50 (2H, m), 2.21 (2H, m), 2.00 (2H, m), 1.41 (2H, m). |
| **19b** | 7.83 (4H, m), 7.37 (4H, m), 6.29 (4H, bs), 2.78 (8H, bs), 1.81 (8H, bs). |
| **19b**[b)] | 7.55 (4H, m), 7.08 (4H, m), 5.97 (4H, s), 2.44 (8H, bs), 1.60 (8H, bs). |
| **19c** | 7.90 (4H, m), 7.37 (4H, m), 6.49 (4H, s), 2.89 (4H, t, 6.0), 2.84 (4H, bs), 1.74 (4H, bs), 1.60 (4H, tt, 10.5 and 6.0), 0.50 (2H, quint, 10.5). |
| **20a** | 7.57 (2H, bd, 8.2), 7.37 (2H, bd, 8.2), 6.91 (4H, m), 6.84 (2H, bd, 7.6), 6.77 (2H, bd, 7.0), 3.64 (2H, m), 3.12 (2H, m), 2.94 (2H, m), 2.37 (2H, m), 2.23 (2H, m), 1.84 (2H, m), 1.65 (2H, m). |
| **20b** | 7.46 (4H, bd, 8.6), 6.97 (4H, dd, 8.6 and 7.2), 6.86 (4H, bd, 7.2), 3.15 (4H, m), 2.40 (4H, m), 1.79 (8H, m). |
| **21a** | 7.20 (2H, bd, 8.1), 7.09 (2H, dd, 8.4 and 2.0), 7.03 (2H, dd, 7.7), 6.83 (4H, bd, 7.8), 6.75 (2H, bs), 2.89 (4H, m), 2.57 (2H, m), 2.32 (6H, m), 1.89 (2H, m). |
| **21b**[c)] | 7.15 (4H, d, 8.4), 6.91 (4H, bd, 8.4), 6.89 (4H, bs), 2.66 (4H, dd, 12.8 and 4.4), 2.28 (4H, dd, 12.8 and 4.4), 1.96 (4H, m), 1.60 (4H, m). |
| **22a** | 7.13 (2H, bd, 8.1), 7.10 (2H, bs), 7.04 (2H, bd, 8.4), 6.93 (2H, bs), 6.86 (2H, dd, 8.4 and 1.8), 6.73 (2H, dd, 8.1 and 1.8), 3.03 (2H, m), 2.82 (2H, m), 2.43 (4H, m), 2.29 (4H, m), 1.72 (2H, m). |
| **22b**[c)] | 7.11 (4H, d, 8.4), 7.02 (4H, bs), 6.79 (4H, bd, 8.4), 2.47 (8H, m), 1.79 (8H, m). |

a) Taken in $CDCl_3$. b) In nitrobenzene-$d_5$. c) NMR data of achiral **21b** and chiral [4.4](2,6)naphthalenophane **22b** were read from the spectrum of the conformer mixture.

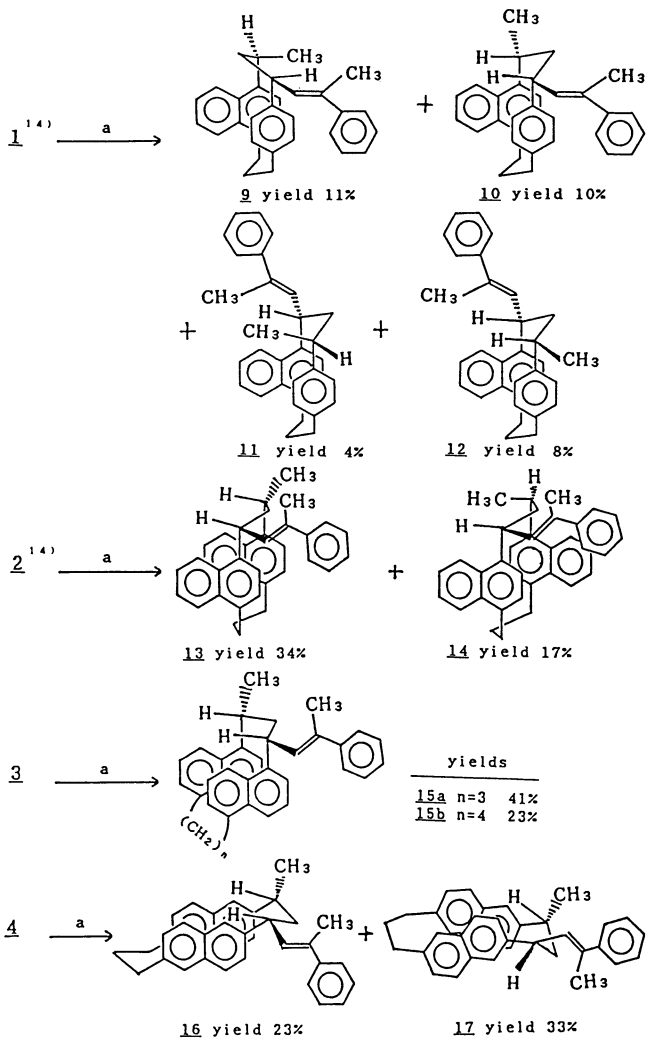



Chart 3. Cationic cyclocodimerization toward [3.*n*]-naphthalenophanes.

is sterically unfavorable,[5] only one possible syn-oriented cation with exo-vinyl group affords exo, cis, syn-isomer **15a**, as observed. The structure of **15b** was determined by the same method as above.[16]

From the reaction mixture of olefin **4a** two isomers of 1-methyl-3-(β-methylstyryl)[3.3](2,6)naphthalenophanes (a 1.0:1.4 ratio and total 56% yield) were isolated by HPLC (Develosil-PYE, MeOH). Compared with reported NMR data of chiral and achiral [3.3](2,6)naphthalenophanes,[10] especially underlined chemical shift(s) for peri-hydrogens in Table 2, compound **16** can be concluded as a derivative of the achiral isomer. An NOE experiment indicates that H-1 and one of the peri-hydrogens (22% NOE enhancement), and also H-3 and another peri-hydrogen (14% NOE enhancement), are in vicinity, so that the disubstituted three-carbon bridge is of cis, exo-configuration. Thus the exo, cis, achiral-structure of **16** is concluded as indicated in Chart 3. Compound **17** can be easily concluded to be a derivative of the chiral isomer, as mentioned above.[10] VT-NMR spectra taken in acetone-$d_6$ from 20 to −90 °C show considerable change at the region of aromatic proton resonance. This change should be the attribute of two conformationally unstable three-carbon linkages, compared with the small change of the aromatic proton peaks of cis-isomer **16**. The fact suggests that **17** has the trans-configuration. The NOE experiment indicates that H-1 and one of the peri-hydrogens are in vicinity (15% NOE enhancement), so that the disubstituted three-carbon bridge must be of exo-configuration. Thus **17** is assigned to the structure depicted in Chart 3. It is interesting that the reaction gave mainly **16** and **17** in an almost equal amount, although eight diastereomers are possible at a random cyclization. This selectivity must be due to the predominant exo-conformation of starting 2-vinylnaphthalene moiety which had already been deduced from the consideration on the chemical shift of methine hydrogen of the 2-vinyl group.[17]

**Synthesis of [4.*n*]Naphthalenophane Derivatives.** Cyclobutane ring is known to be cleaved regioselectively by electron-transfer reduction like Birch one.[18] The ring cleavage of naphthalenophanes **5—8** becomes ultimately a general synthetic method of [4.*n*]naphthalenophanes which are prepaced only in low yields by other ones reported previously.

Treated under the usual Birch reduction conditions, naphthalenophanes **5—8** gave several over-reduced products. $^1$H NMR spectroscopic analysis of the products showed olefinic hydrogens which were generated by the reduction of naphthalene rings. In order to obtain desired naphthalenophanes from them, the reduced material were oxidized in decalin with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 170 °C. Yields are shown in Chart 4.

The sequence of reactions is depicted in Chart 4. The products were easily isolated by column chromatography ($SiO_2$, benzene/cyclohexane), purified by recrystallization from hexane, and characterized mainly by $^1$H NMR spectroscopy. Analytical and spectroscopic data are listed in Tables 1 and 2.

From naphthalenophanes **7**, products **20** were obtained without conformational alteration of naphthalene nuclei, whereas **6** gave conformationally stable *anti*-naphthalenophanes **19** exclusively. Compound **8a** (the chiral/achiral isomer ratio=4.2) gave two isomeric [3.4](2,6)naphthalenophanes **21a** and **22a** (chiral **22a**/achiral **21a** isomer ratio=4.2), which were isolated by HPLC ($SiO_2$, hexane). These structures were determined by $^1$H NMR spectroscopy, just as done for compounds **16** and **17**.

Compound **19a** did not change the chemical shift of intraannular hydrogens even at 200 °C. Therefore it is concluded that the naphthalene ring rotation in the ring system needs very high activation energy. On the other hand, compound **19b** showed the coalescence

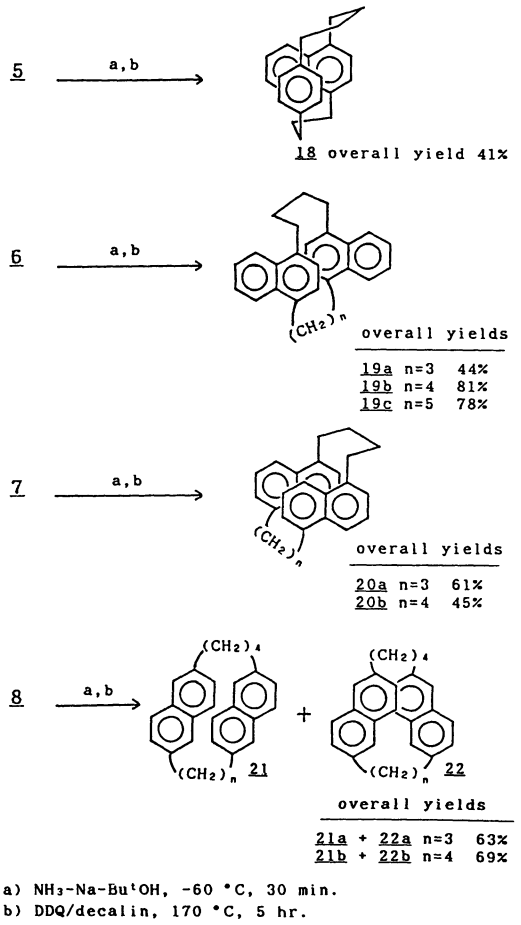



Chart 4. Birch reduction toward [4.$n$]naphthalenophanes.

of intraannular aromatic hydrogens of its syn and anti conformers at 10±5 °C. The rotation barrier at the coalescence temperature is calculated 13 kcal mol$^{-1}$. Chiral naphthalenophane **22a** was heated at 200 °C for 12 h, but there occurred no isomerization to achiral **21a** by the ring rotation, according to the HPLC analysis. On the other hand, naphthalenophanes **8b** gave conformationally fluxional [4.4](2,6)naphthalenophanes **21b** and **22b**. The conformer ratio (chiral/achiral) at r.t. was 2.4:1. Naphthalenophanes **21b** and **22b** showed the coalescences of aromatic and aliphatic hydrogens at 175±5 °C, and the rotation barrier is calculated 22 kcal mol$^{-1}$.

## Discussion

Among several synthetic methods for structurally interesting naphthalenophanes, the present methods have an advantage; i.e., a single starting material for [2.$n$]-, [3.$n$]-, and [4.$n$]naphthalenophane skeletons. When one needs a large amount of naphthalenophanes, the methods using vinylnaphthalene derivatives will be an unignorable one.

The syn selectivity of the methods mentioned here has a great advantage, because syn isomers are generally conformationally unstable and given as minor products by ordinary methods. By using this advantage of the syn selectivity the room required for the intraannular rotation of naphthalene nuclei was determined. By the enlargement of the ring system from [2.3] to [4.4] one, the (1,5)naphthalenophanes always kept syn conformation under the experimental conditions of −60 °C to 180 °C, because quite a large volume is necessary if the nucleus rotates around the axe through C1 and C5 of naphthalene ring.

Interestingly the (1,4)naphthalenophanes showed the point for the nuclei to start the rotation within [2.3] to [4.5] system. Namely [3.4](1,4)naphthalenophane takes only anti-conformation after the transformation of *cis,exo*-1,2-ethano-*syn*-[2.3]naphthalenophane **6a**, whereas *syn*-[3.3] and [2.4]naphthalenophane take only syn-conformation upto their melting points. The room requirement for the rotation of naphthalene rings is just similar to that previously reported for [$n.m$]paracyclophanes:[19] i.e., activation free energies for [3.4]- and [4.4]paracyclophanes are reported 33 kcal mol$^{-1}$ at 160 °C and 15 kcal mol$^{-1}$ at ca. 15 °C, respectively. From the coalescence temperatures, activation free energies for **19a** and **b** were calculated ≥25 kcal mol$^{-1}$ (≥200 °C) and 13 kcal mol$^{-1}$ (10 °C), respectively.

This is the first report on the naphthalene ring rotation in the skeletons of the (2,6)naphthalenophanes. The ring rotation barrier for [4.4](2,6)naphthalenophane exceeds that of [4.4](1,4)naphthalenophane by 9 kcal mol$^{-1}$.

## Experimental

**General.** Elemental analyses were done at the Microanalysis Center of Kyoto university. Melting points are not corrected. NMR spectra were recorded on a Varian XL200 FT-NMR spectrometer. IR spectra were taken on a JASCO IR-810 infrared spectrophotometer. Mass spectra were recorded on a Hitachi M-80A mass spectrometer. High performance liquid chromatographic analyses (HPLC) were carried out by using Altex Model 100A and Knauer 64 pumps with a Hitachi wavelength tunable effluent monitor and a Shimadzu SPD-6A UV spectrophotometric detector.

Solvents like benzene, THF, and ether were distilled over sodium diphenylketyl after prolonged reflux. Other commercially available highest-grade reagents were used without further purification. Monomers were prepared conveniently by our methods depicted in Chart 1.[12]

**Synthesis of 1,2-Ethano[2.4](1,5)naphthalenophane 7b (General Procedure).** A 1-l Pyrex flask equipped with a magnetic stirrer, reflux condenser, and $N_2$ inlet was placed 4.28 g (11.8 mmol) of 1,4-bis(5-vinyl-1-naphthyl)butane **3b** dissolved in 900 ml of dry benzene under $N_2$. It was irradiated by a high-pressure mercury lamp (400 W) for 17 h. Then benzene was removed by evaporation. Reaction mixture dissolved in 20 ml of dry THF was transferred to 50-ml two-necked flask equipped with a magnetic stirrer, dropping funnel, and $N_2$ inlet. A 10 ml of $B_2H_6$-THF complex (0.1 M) was added to it slowly at r.t. After stirred for 12 h at r.t., THF was removed and products were isolated by column chromatography ($SiO_2$, hexane). Recrystallization

from benzene-methanol gave 1.41 g (33%) of *cis,exo*-1,2-ethano-*syn*-[2.4](1,5)naphthalenophane.

**Synthesis of *cis,exo*-1-Methyl-3-(β-methylstyryl)[3.3](1,5)-naphthalenophane 15a (General Procedure).** A 1-l, four-necked round-bottomed flask was equipped with a magnetic stirrer, thermometer, and $N_2$ inlet was placed 2.36 g (6.78 mmol) of 1,3-bis(5-vinyl-1-naphthyl)propane **3a** and 3.9 ml (36.2 mmol) of 2-phenylpropene which were dissolved in 566 ml of dry benzene under $N_2$ at 50 °C. Trifluoromethanesulfonic acid (0.01 g, 0.068 mmol) was dissolved in 1 ml of dry benzene and added at once to initiate the reaction under vigorous stirring. After stirred for 30 min, 200 ml of 10% aqueous NaOH was added to stop the reaction. The reaction mixture was washed with 200 ml of water 3 times and dried anhydrous $Na_2SO_4$. After the reaction mixture was filtered and benzene was removed, products were isolated by column chromatography ($SiO_2$ , benzene-hexane). Recrystallization from benzene-methanol gave 0.73 g (41%) of the title compound as the sole naphthalenophane derivative.

Compound **15** can be isolated by crystallization after the column chromatography. The purity of so-crystallized **15** was usually 95%. Compound **16** and **17** can be separated from each other by MeOH extraction. From the MeOH solution **17** was crystallized and purified up to 90%. From the MeOH-insoluble part **16** was purified up to 95% by recrystallization from EtOH.

**Synthesis of *syn*-[4.4](1,5)Naphthalenophane 20b (General Procedure).** A 200 ml, three-necked round-bottomed flask equipped with a magnetic stirrer, $N_2$ inlet, and gas inlet was cooled by Dry Ice-methanol bath at ca. −50 °C. Ammonia gas was introduced into the system. When ca. 100 ml of liquid ammonia was condensed, the gas inlet tube was replaced with a glass stopper. About 1 g of Na was added carefully piece by piece into liquid ammonia and stirred for 10 min. *cis,exo*-1,2-Ethano-*syn*-[2.4](1,5)-naphthalenophane **7b** (500 mg, 1.38 mmol) and 2 ml of *t*-butyl alcohol dissolved in 20 ml of dry THF were added slowly in it, and the mixture was stirred for 30 min. Then the excess Na was consumed by cautious addition of 10 ml of water. The ammonia was allowed to evaporate itself slowly in a hood. Then products were extracted by 20 ml of benzene. The benzene extract was washed with 20 ml of water three times and dried over anhydrous $Na_2SO_4$. After filtration, benzene was removed, products were isolated by column chromatography ($SiO_2$, benzene-hexane). The yield was 350 mg. A 50 ml flask equipped with a magnetic stirrer, reflux condenser, and $N_2$ inlet was placed 200 mg of the Birch reduction products and 300 mg (1.32 mmol) of DDQ were dissolved in 30 ml of decalin under $N_2$. The reaction mixture was heated with stirring at ca. 180 °C for 12 hours. After removed the decalin, products were isolated by column chromatography on $SiO_2$ (benzene-hexane). Recrystallization from benzene gave 130 mg (0.036 mmol, a 45% yield) of *syn*-[4.4](1,5)naphthalenophane.

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