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CATIONIC CYCLOCODIMERIZATION. 2.[1] SYNTHESES OF [3.3](1,4)NAPHTHALENOPHANE AND [3.3]PARACYCLO(1,4)NAPHTHALENOPHANE DERIVATIVES

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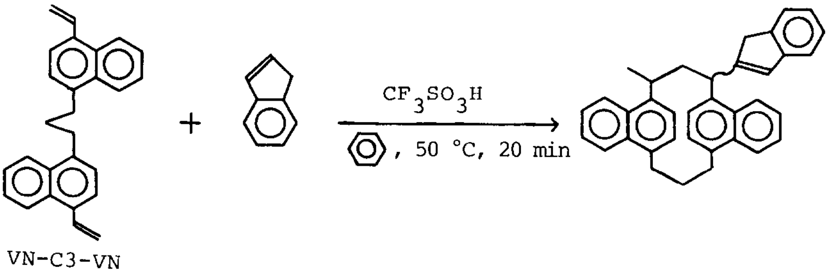
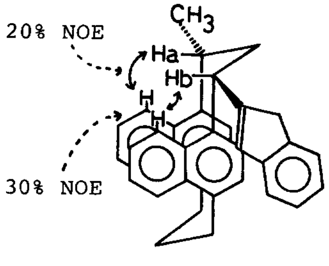
Abstract: 1,3-Bis(4-vinylnaphthyl)propane and 1-(4-vinylnaphthyl)-3-(p-vinylphenyl)propane, were cyclocodimerized with indene to afford indenyl-substituted [3.3](1,4)naphthalenophanes and [3.3]paracyclo(1,4)naphthalenophanes.

Syntheses of [3.3](1,4)naphthalenophane[2] and [3.3]paracyclo(1,4)naphthalenophane[3] are not so facile that it is attractive to clarify the applicability of the cyclocodimerization[1] to the syntheses of these molecular frames. In fact, by the treatment of easily available 1,3-bis(4-vinylnaphthyl)propane (VN-C3-VN)[4] and 1-(4-vinylnaphthyl)-3-(p-vinylphenyl)propane (VN-C3-St)[5] with indene under the cyclocodimerization conditions, we obtained the corresponding phanes in reasonable yields.

VN-C3-VN (0.024 M) and indene (0.04 M) were dissolved in absolute benzene. Into the mixture, CF_3SO_3H-benzene solution (0.2 mM) was added all at once at 50°C under vigorous stirring. After 20 min, the reaction was stopped by the addition of 10 ml of 10% NaOH. The reaction mixture was washed three times with water, dried over Na_2SO_4, and condensed by evaporation. Cyclocodimers were isolated from polymeric materials as a mixture in 20.0% yield by column chromatography (SiO_2, cyclohexane-benzene). Isomers were separated by reversed-phase HPLC (Cosmosil C-18, methanol). The cyclocodimerization of VN-C3-St with indene was carried out in the same way as above except that, in the separation by reversed phase HPLC, Develosil-PYE column[6] was used with methanol as eluent. The products were certified to be [3.3](1,4)naphthalenophane and [3.3]paracyclo(1,4)naphtha-





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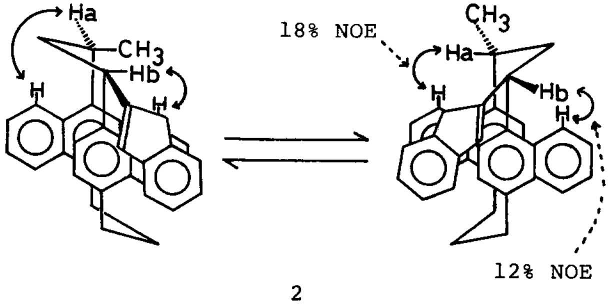

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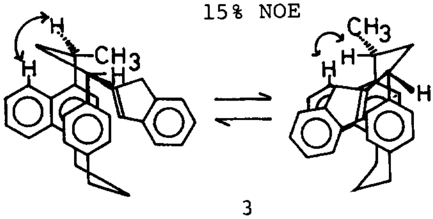
lenophane derivatives by ^{1}H-NMR, UV, VIS of their TCNE-complexes, IR, MS, and elemental analysis (see Table).

The cationic cyclocodimerization of VN-C3-VN with indene formed two crystalline [3.3](1,4)naphthalenophane derivatives.[7] One has a mp 246-7 °C and is proved to be a syn isomer (15.3% yield) by the ^{1}H-NMR analysis.[2] Particularly, the nuclear Overhauser effect (NOE)[8] can determine the structure strictly: mild irradiation at Ha or Hb caused the increase of integral of one peri-hydrogen resonating at δ 7.72 or at δ 7.77, respectively. Out of four plausible isomers *exo*-{*cis*-[1-(2-indenyl)-3-methyl]}-*syn*-[3.3](1,4)naphthalenophane 1,[9] can explain this NOE, but the others can not. Another isolated product which has a mp 203-4 °C and is proved to be an anti isomer (4.7% yield) by ^{1}H-NMR shows the similar NOE to the syn isomer. This NMR evidence excludes three structures out of four plausible anti isomers, and, consequently, *exo*-{*trans*-[1-(2-indenyl)-3-methyl]}-*anti*-[3.3](1,4)naphthalenophane 2 is concluded to be the product.

The other α,ω-diene, VN-C3-St gave four crystalline [3.3]paracyclo(1,4)naphthalenophane derivatives, when it was cyclocodimerized with indene.[10] The ^{1}H-NMR chemical shifts of methylene hydrogens of the indenyl groups in these phanes are affected remarkably by the neighboring aryl groups,[11] so that it is easy



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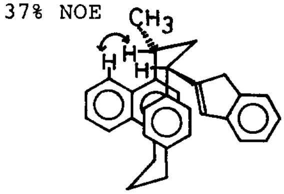

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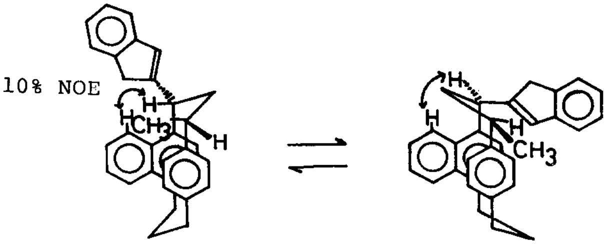

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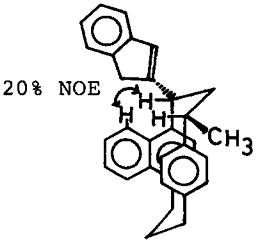

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to determine which group, vinylnaphthyl(VN)- or vinylphenyl(St)-group, was first protonated. The cis, trans configuration was determined based upon the chemical shifts of methyl group as well as the methine group bearing the methyl group.[1]

As major isomers, two phanes originated from the protonation on the VN group were isolated. Their structures were determined by NOE to be *endo*-{*trans*-[1-(2-indenyl)-3-methyl]}[3.3]paracyclo(1,4)naphthalenophane **3** (12.4% yield, mp 105-8 °C) and exo-cis isomer **4** (10.5% yield, mp 162-4 °C). The structures of other minor isomers, which were produced by the initial protonation on the St group, were also clarified by NOE to be *exo*-{*trans*-[1-methyl-3-(2-indenyl)}[3.3]paracyclo(1,4)naphthalenophane **5** (4.2% yield, mp 144-7 °C) and exo-cis isomer **6** (3.8% yield).[12]

Consequently, we would like to stress that the cationic cyclocodimerization that was first developed for the synthesis of [3.3]paracyclophanes can also be a quite facile method of constructing multi-nuclear phanes like [3.3](1,4)naphthalenophanes and [3.3]paracyclo(1,4)naphthalenophanes from easily available olefins

Table Spectroscopic Data of Phanes

	^{1}H-NMR, δ in ppm[a]			IR[b]	FS[c]	VIS[d]	MS	Anal (Found)[e]
	H1	H2	Me (d, J in Hz)	(cm^{-1})	(nm)	(nm)	(M$^{+\cdot}$, m/z)	C : H
1	6.80	3.17	1.40 (6.8)	833	464±2	770±5	464	93.06(92.76):6.94(6.98)
2	6.00	3.24	1.49 (6.8)	833	-[f]	724±5	464	-[g]
3	5.91	3.18	1.59 (7.1)	824	368±2	697±5	414	92.71(92.74):7.29(7.39)
4	5.79	3.16	1.41 (6.9)	824	370±2	680±5	414	92.71(92.91):7.29(7.34)
5	5.91	3.33	1.35 (7.0)	821	371±2	648±5	414	-[h]
6	5.80	3.29	1.33 (6.9)	820	372±2	648±5	414	-[i]

a Recorded by a Varian T-60A NMR spectrometer in $CDCl_3$, using TMS as an internal standard. H1 designates phenyl protons (for **3** to **6**) or protons at C-2 and C-3 positions of naphthalene rings (for **1** and **2**). H2 designates methylene protons of indenyl group.

b KBr-disk method. The out-of-plane vibration of C=C double bond.

c In a nitrogenated cyclohexane.

d Charge-transfer band of CT complex of a phane with TCNE in CH_2Cl_2.

e Analyzed at the Microanalysis Center of Kyoto University.

f Complex; see J. Nishimura, M. Furukawa, S. Yamashita, T. Inazu, and T. Yoshino, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3257 (1981).

g High resolution mass spectrum, m/z 464.2473 ($M^{+\cdot}$, calcd 464.2504).

h High resolution mass spectrum, m/z 414.2332 ($M^{+\cdot}$, calcd 414.2347).

i See ref. 12.

like VN-C3-VN and VN-C3-St. The syntheses of other multi-nuclear phanes are now in progress.

References and Notes

1. Part 1; J. Nishimura, K. Hashimoto, T. Okuda, H. Hayami, Y. Mukai, and A. Oku, *J. Am. Chem. Soc.*, **105**, 4758 (1983).
2. T. Kawabata, T. Shinmyozu, T. Inazu, and T. Yoshino, *Chem. Lett.*, **1979**, 315.
3. T. Otsubo, M. Kitasawa, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **52**, 1515 (1979).
4. J. Nishimura, Y. Ishida, K. Hashimoto, Y. Shimizu, A. Oku, and S. Yamashita, *Polym. J.*, **13**, 635 (1981).
5. J. Nishimura and S. Yamashita, "Cyclopolymerization and Polymers with Chain-Ring Structures," ed. by G. Butler and J. E. Kresta, Am. Chem. Soc. Symp. Series No 195 (1982).
6. We are grateful to Dr. Nobuo Tanaka, Kyoto Institute of Technology, for providing the column. N. Tanaka, Y. Tokuda, K. Iwaguchi, and M. Araki, *J. Chromato.*, **239**, 761 (1982).
7. The similar naphthalenophane derivatives were obtained by the reactions with styrene, 2-phenylpropene, and 1,1-diphenylethylene, in 53.6, 51.6, and 16.9% yields, respectively. The detailed structural elucidation of these phanes is in progress.
8. Determined by a Varian XL 200 FT-NMR spectrometer in nitrogenated $CDCl_3$, using TMS as an internal standard.
9. The designation of endo- and exo-conformation of the bridging methylene group is made for the conformer having indenyl group in a quasiequatorial position. In exo isomer, the middle methylene group of the 1,3-disubstituted bridge directs opposite to the peri-hydrogen of the naphthyl group nearest to the indenyl group.
10. The similar paracyclonaphthalenophane derivatives were obtained by the reactions with styrene, 2-phenylpropene, and 1,1-diphenylethylene, in 20.7, 33.5, and 27.0% yields, respectively. The detailed structural elucidation of these phanes is now in progress.
11. The methylene protons of the indene ring of *cis*-[1-(2-indenyl)-3-methyl]-[3.3]paracyclophane and those of **2** resonate at δ 3.18 and 3.24, respectively, and the chemical shifts were used as the reference for the structural assignment of paracyclonaphthalenophane derivatives. The corresponding chemical shifts of the derivatives are listed as H2 in Table.
12. This was obtained in a relatively low yield as the very last effluent from HPLC of which peak overlapped with that of **5**. Therefore, it was difficult to be isolated in the pure state even by means of HPLC. It contained 24% of **5** after recrystallization from ethanol; mp 92 - 6 °C (mixture).

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