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INTRAMOLECULAR [2 + 2] PHOTOCYCLOADDITION. 9.[1]

STEREOSELECTIVE SYNTHESIS OF NAPHTHALENOPHANES AND EFFECTS OF THE TETHER LENGTH AND SUBSTITUENTS ON THE PHOTOCHEMICAL REACTION COURSES OF VINYLNAPHTHALENES[2]

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Abstract: The photocycloadditions of vinylnaphthalenes 1 to naphthalenophanes 5 - 8 were affected significantly by the length of tethers between naphthalene rings and by substituents at vinyl groups.

Vinylarenes have been extensively studied in the synthesis of cyclophanes by means of [2 + 2] photocycloaddition.[3] We recently found highly stereoselective reactions of olefins 1 toward several naphthalenophanes like 5 to 8. The selectivity seems to primarily attributed to the conformational rigidity of olefinic substituents on the C-1 position of the naphthalene ring. We now report herein these reactions, focusing on their synthesis and effects of the tether length and substituents.

Reaction conditions, yields, and physical properties of products are

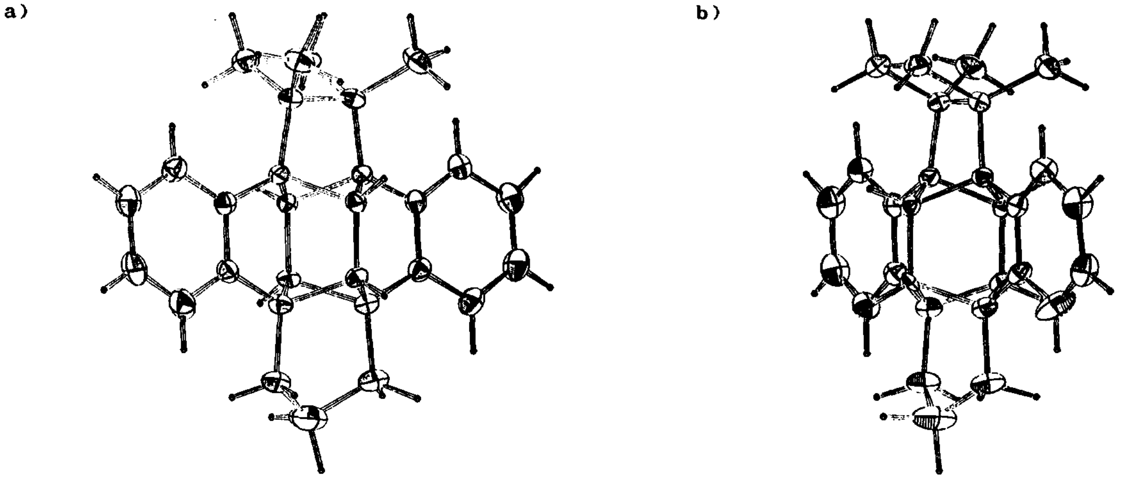
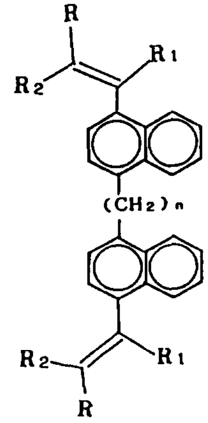


Figure 1 ORTEP drawing of the structure of 4 (R=0.088).
Figure b) shows the structure turned 15° around Y axe from Figure a). Thermal ellipsoids are at 50% probability level for carbon atoms. The hydrogen atoms are shown as the points. The estimated standard deviations for bond distances lie between 0.003 and 0.007 Å.

Table I Preparation of Naphthalenophanes[a]

	Olefin					Reaction Time, h	Product	Yield, %	Mp, °C	Anal. Calcd (Found) C, %; H, %
	n	R	R_1	R_2	mM					
1a	3	H	Me	H	8	24	4	21	167-8	92.50(92.40); 7.50(7.59)
1b	4	H	Me	H	12	24	5b	6	127-9	92.26(92.30); 7.74(7.66)
1c[b]	5	H	Me	H	10	36				
1d[b]	3	H	Ph	H	2	36				
2	3	H	Me	H	6	24	6	1	47-8	91.97(91.70); 8.03(7.97)
3a	3	H	Me	H	6	24	7	15	133-4	92.50(92.46); 7.50(7.48)
3b[b]	4	H	Me	H	4	24				
1e	3	Me	H	H[c]	5	13	8a	18	202-3	92.50(92.65); 7.50(7.27)
1f	4	Me	H	H[c]	10	36	8b	17	187-8	92.26(92.04); 7.74(7.90)
1g	3	iPr	H	H[c]	10	12	8c	24	158-9	91.61(91.83); 8.39(8.17)
1h[b]	3	tBu	H	H[c]	10	24				
1i	3	Ph	H	H[c]	4	12	8d	24	102-3	93.56(93.65); 6.44(6.35)
1j[b]	3	Me	Me	H[c]	5	16				
1k[b]	3	H	Me	Me	8	12				
1l	3	COOMe	H	H[c]	5	18	8e	76	212-4	80.15(79.87); 6.07(6.26)

[a] Reaction conditions: in benzene through a Pyrex filter with a 400 W high pressure mercury lamp. See ref. 3b and d for the detailed procedure. [b] No naphthalenophanes were obtained. [c] At photostationary state R_2 should be equal to R.



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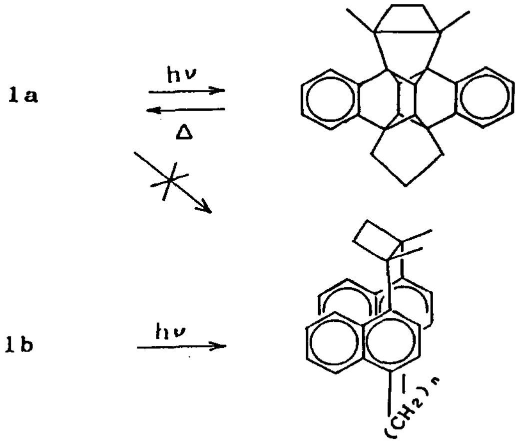

(1)

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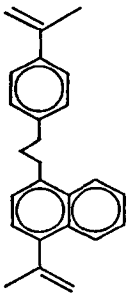

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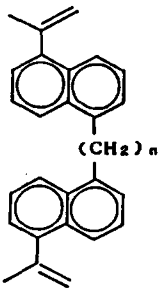

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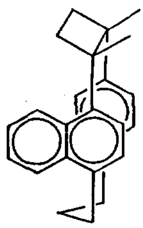

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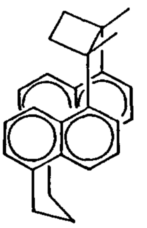

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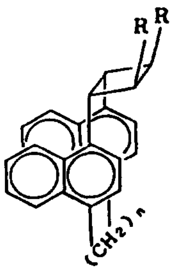

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summarized in Table I. The yields are fair for these structurally interesting materials, compared with those of other synthetic methods.[4,5]

Under irradiation, olefin 1a formed cage compound 4 instead of naphthalenophane 5a, although its regioisomer 3a gave the expected one 7 (vide infra). Compound 4 showed an attractive photochromism and underwent the thermal cycloreversion to 1a. The cycloreversion cleanly proceeded without any byproducts, so that we were prompted to measure the rate. The first-order rate constant (k_1) was 0.948x10^{-4} s^{-1} at 110 °C, 2.77x10^{-4} s^{-1} at 120 °C, 6.34x10^{-4} s^{-1} at 130 °C, 16.1 x10^{-4} s^{-1} at 140 °C, and 35.6x10^{-4} s^{-1} at 150 °C. The thermodynamic parameters are as follows: $\Delta H^{\ddagger}$ = 28.3 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = -3.63 ± 0.07 e.u., and $\Delta G^{\ddagger}{}_{110\,°C}$ = 29.6 ± 0.3 kcal/mol. Since no intermediates were detected in the reaction mixture by ^{1}H NMR spectroscopy, this reverse process could be concerted or rapidly stepwise.

The structure of 4 was determined by X-ray crystallography, whose ORTEP drawing is depicted in Figure 1.[6] It has the very intriguing structure generated formally through doubly occurred [π4s + π2s] reaction, during the [π2s + π2s] cycloaddition of 2-propenyl groups, although there have not been any conclusive evidences on whether these processes occur in a concerted or stepwise mechanism. This transannular reaction product is structurally similar to dibenzoequinene obtained from anti-[2.2](1,4)naphthalenophane.[7,8] Generally speaking, however, naphthalenophanes are apt to give products of singly occurred [π4s + π4s] reaction under photoirradiation.[9] Therefore it is one of the uncommon examples in the photoreaction of naphthalenophanes.

Yet reaction (1) became not to proceed at all under the same reaction conditions, when tetramethylene was used as the tether like in monomer 1b. Alternatively reaction (2) took place to afford naphthalenophane 5b in a 6% yield. The structure of 5b is of the endo configuration for the cyclobutane ring system. This endo,cis-isomer is not actually the least strained one among possible isomers,[10] but the second highest strained one, according to the MM2 calculation. As one of the explanations, it is believed that the small difference of the bulkiness between methyl (Me-C=) and methylene (-C=CH$_2$) groups determines the reaction path. The kind of cyclization (2) also occurred with olefins 2 and 3a.

When the longer methylene chains were used as the tether (1c and 3b), photoirradiation of the α-substituted olefins did not give any cycloadducts or naphthalenophane derivatives. This seems to be due to the loss of entropy advantage.[3c] Eventually it is notable that only one methylene group difference at the tether dramatically changed the reaction course from the transannular one, via the normal [2 + 2] cycloaddition,[3b] to none of intramolecular cyclizations.

Substituents at the vinyl β-position show apparent steric hindrance on this photocyclization. The introduction of two alkyl R,R$_1$- or R$_1$,R$_2$-substituents (1i and 1k) completely prevented it from occurring, even if they are small methyl groups. The R-substituents affected it less significantly than the above ones; i.e., olefin 1h with isopropyl groups gave naphthalenophane 8d in a 24% yield. The reaction, however, did not proceed with t-butyl groups (1h). This is attributed to the extremely high strain loaded on the cyclobutane ring at the cyclization. Phenyl[11] and carbomethoxy group[12] for R substituents gave desired naphthalenophanes in reasonable yields. When R substituents are bigger than and equal to methyl group, trans-isomers 8 are obtained exclusively.

Detailed mechanistic and further synthetic works are now in progress and will be reported elsewhere.

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References and Notes

1) Dedicated to Professor Dr. Rolf Huisgen, Munich, on the occasion of his 70th birthday.

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4) As a review, see "Cyclophanes I and II", ed. by P. M. Keehn and S. M. Rosenfeld, Academic Press, New York, 1983.

5) The structural analyses of the products were carried out with several NMR spectroscopic methods, including NOESY and COSY, and all results are well consitent with their structures.

6) Crystallographic study of 4. C29H28, M = 376.54. The crystal belongs to the monoclinic system, space group $P2_1/n$, Z=4. Cell parameters: a =19.668 (7), b = 14.231 (6), c = 7.200 (3) Å, β = 100.20° (3), V = 1983.2 Å^3, d_c=1.22 gcm^{-3}, λ(MoKα) = 0.71073 Å. Diffractometric intensity data were obtained from a crystal of 0.4 x 0.3 x 0.3 mm. From the 4073 unique reflections collected by the $\omega - 2\theta$ scan-technique up to $2\theta = 60°$, only 2922 were considered as observed having $F_o \geq 3.0\sigma(F_o)$ and kept in refinement calculations. The structure were solved by direct methods and refined by least-squares minimizing the function $\Sigma w(\Delta F)^2$. Most of the hydrogen atoms were located on difference Fourier maps. Final conventional R factor was 0.088.
List of the atomic coordinates, bond distances and angles, and structure factors, have been deposited at the Cambridge Crystallographic Data Centre, U.K. as Supplementary Material.

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8) The similarity does not directly mean that the anti-naphthaleneophane analogue should exist in the reaction mixture, because there is another possibility to explain the formation of 4; i.e., compound 4 can be formed from the rotation of a naphthalene ring during [2 + 2] cyclization of propenyl groups. The latter explanation is supported by the formation of 5b in reaction (2) and the mobility of the ring in the [3.4](1,4)naphthalenophane.[3c]

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10) As 1,1,2,2-tetrasubstituted cyclobutane derivatives, endo,cis-, exo,cis-, and trans-isomers are possible, and a 1,1,3,3-tetrasubstituted one is also possible. Total four isomers are conceivable.

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