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Synthesis of Paddlanes Possessing Cyclophane Shaft and Cyclobutane Blades

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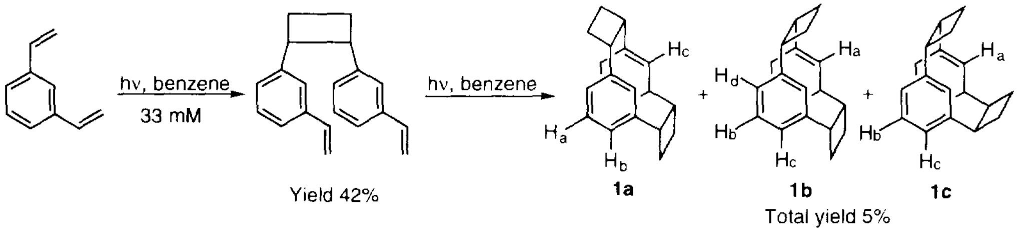
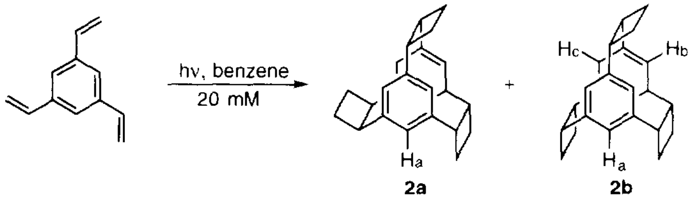
Abstract: 1,2- And 1,2,4,5-paddlanes were successfully prepared by the intermolecular [2 + 2] photocycloaddition of *o*-divinyl- and 1,2,4,5-tetravinylbenzenes, respectively. On the other hand, no desired paddlanes were obtained from *p*-divinyl- or 1,2,3-trivinylbenzene. The structural features of the obtained paddlanes were examined by UV and ^{1}H NMR spectroscopy. © 1997 Elsevier Science Ltd.

INTRODUCTION

The paddlanes, dealt with in this work, are multi-bridged cyclophanes with cyclobutane rings, and their ultimate goal is the hexa-bridged one, so-called superpaddlane. In the early works, tetraphenyl-substituted 1,3-paddlanes[1] and hexaphenyl-substituted 1,3,5-paddlanes[2] were synthesized by intermolecular photocycloaddition of corresponding stilbene derivatives and characterized by X-ray crystallography.[3] The parent compounds, however, had not been reported before we started the works,[4,5] in which they could be successfully prepared by the [2 + 2] photodimerization of *m*-divinyl-[4] and 1,3,5-trivinylbenzenes.[5] As shown in Eq. 1, *m*-divinylbenzene, irradiated with a high-pressure mercury lamp and Pyrex filter in benzene, afforded 1,3-paddlanes **1** in 5% yield with three isomers in a ratio of 5:10:3.[4] Since an intermediate, *cis*-1,2-bis(*m*-vinylphenyl)cyclobutane, was obtained in 42% yield, this reaction undoubtedly proceeds stepwise. 1,3,5-Paddlane **2** was synthesized from 1,3,5-trivinylbenzene in a similar manner (Eq. 2).[5] The isomer ratio was 26/74 and total yield was 1%.[5]



(1)



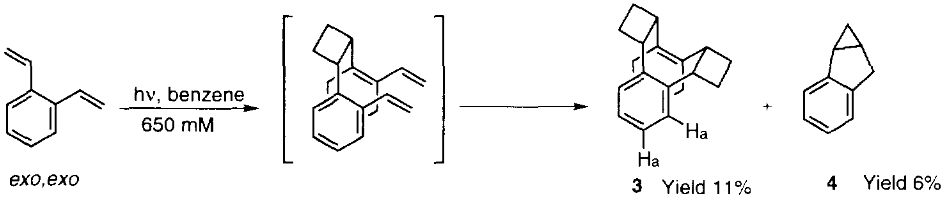
(2)

Total yield 1%

Since we achieved those previous target paddlanes, we have studied to find the scope and limitation of this method, hoping to establish a reasonable route to the superpaddlane. In this paper, we would like to report the synthesis and properties of 1,2- and 1,2,4,5-paddlanes and to reveal the limitations of this intermolecular photocycloaddition as a synthetic method.

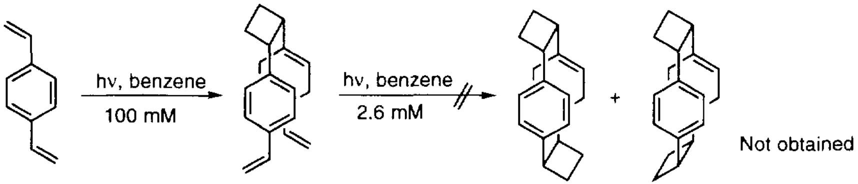
RESULTS AND DISCUSSION

It was reported that *o*-divinylbenzene afforded indane derivative **4** by the intramolecular photocyclization, but the formation of 1,2-paddlane **3** was not mentioned in this study.[6] Since the reaction conditions, especially the olefin concentration applied previously, were not suitable for the intermolecular [2 + 2] photocycloaddition toward **3**, we reexamined the photoreaction of this olefin. At this time, this reaction was carried out in benzene under a rather concentrated condition (650 mM) using a high-pressure mercury lamp through a Pyrex filter (Eq. 3). Surprisingly, we obtained 1,2-paddlane **3** in 11% yield, which actually had two *cis*-cyclobutane rings directed to exo of each other, among the conceivable three stereoisomers. The other paddlanes possessing a cyclobutane ring directed to endo were not obtained at all, due to the steric repulsion between the cyclobutane moieties and the predominant exo,exo-conformation of the starting *o*-divinylbenzene in the ground state (NEER principle).[4,7-10] Indane derivative **4** was also produced in 6% yield. In the course of the reaction, a half-cyclized dimer was detected as an intermediate by ^{1}H NMR spectroscopy, in which the vinyl protons were high-field shifted (0.3–0.4 ppm) relative to those of *o*-divinylbenzene. This result suggests again that the reaction apparently proceeds stepwise.



3 Yield 11% **4** Yield 6% (3)

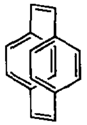
p-Divinylbenzene, irradiated in benzene under conditions similar to the above, afforded *cis*-1,2-bis(*p*-vinylphenyl)cyclobutane **5** in 28% yield (Eq. 4). Further photoirradiation resulted only in the consumption of **5** without the formation of desired 1,4-paddlanes, under any irradiation conditions including photosensitization by triplet benzophenone.



5 Yield 28% (4)

Since [2.2]cyclophan-1,9-diene **6**,[11] 1,2;9,10-dimethano[2.2]- **7**,[12] and 1,2-ethano-9,10-methano[2.2]paracyclophanes **8**[13] were successfully prepared, it seems unlikely that the 1,4-paddlane is heavily strained. Actually the strain energy (Est) is calculated as 105 kcal/mol and the energy of the cyclophane part (ΔEst = 105.4 - 2x28.7 (cyclobutane ring strain) = 48.0) is almost equal to that of parent [2.2]paracyclophane (50 kcal/mol). Moreover, according to Hasegawa and his associates,[14] substituted 1,4-paddlane **9** was topochemically produced under the irradiation of longer-than-350-nm light.

These facts mean that the failure to form 1,4-paddlanes is due to the kinetic reasons. That is, the benzene rings in **5** are too stiff to combine the two vinyl groups into a cyclobutane ring within the lifetime of its excited state[15] in solution. In solid state,[14] however, the first cyclization occurs in the crystalline lattice formed by monomeric olefins and the cell cavity cannot become large enough even after the first cyclization, due to the lattice energy, so that the remaining two vinyl or olefinic groups can be close enough to accept the second cyclization leading to desired 1,4-paddlane derivatives **9**. Unfortunately, *p*-divinylbenzene is a heavy oil at room temperature, and we have not so far successfully carried out its photochemical reaction in solid state at -78 °C.



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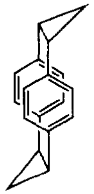

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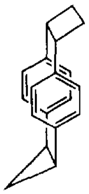

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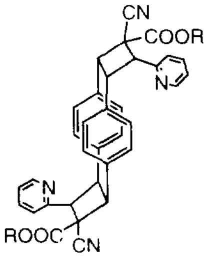
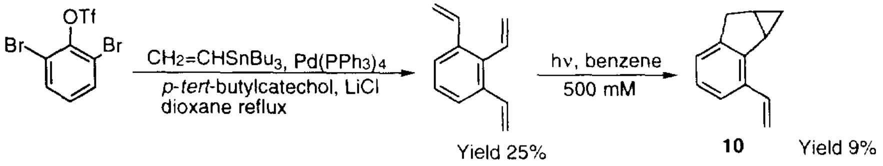


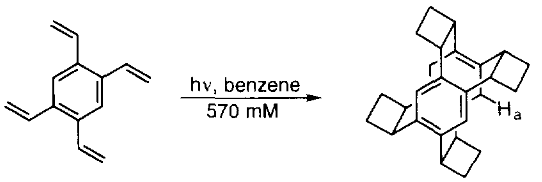
9

1,2,3-Trivinylbenzene was synthesized from 2,6-dibromophenol by the sequence of sulfonylation with triflic anhydride and coupling with tributylvinyltin.[16] When the olefin was photoirradiated in the usual manner, only indane derivative **10** was formed by the intramolecular photoreaction as an isolated product, but no desirable paddlane was detected (Eq. 5). It is because we cannot avoid the contribution of the exo,endo-divinyl conformation in this olefin, which is favorable for the formation of an indane derivative.



(5)

1,2,4,5-Tetravinylbenzene was synthesized by the method reported.[17] This olefin was irradiated in benzene under conditions similar to those mentioned above, affording 1,2,4,5-paddlane **11** in 0.6% yield (Eq. 6). According to ^{1}H NMR spectroscopy, the cyclobutane rings are directed to the opposite side of that in the *ortho*-position. The extremely low yield seems to be attributed to the high strain loaded at the transition state.



11 Yield 0.6% (6)

In Fig. 1, the UV spectra of 1,2- and 1,2,4,5-paddlanes (**3** and **11**) in cyclohexane are illustrated. Since the two benzene rings of **3** open widely with an angle of 64° according to the MM2 calculations, **3** is hardly regarded as a cyclophane of ordinary syn-configuration. Therefore, its benzenoid band is not so much red-shifted from that of the reference *o*-xylene. Nevertheless, it absorbs ultraviolet light of slightly longer wavelength than *o*-xylene, and also shows the broad benzenoid bands. These features are characteristic of an orthocyclophane. On the other hand, paddlane **11** is a fully overlapped cyclophane, so that it absorbs light up to 340 nm. Especially, its benzenoid band is much broadened and red-shifted by ca. 45 nm from that of the reference durene.

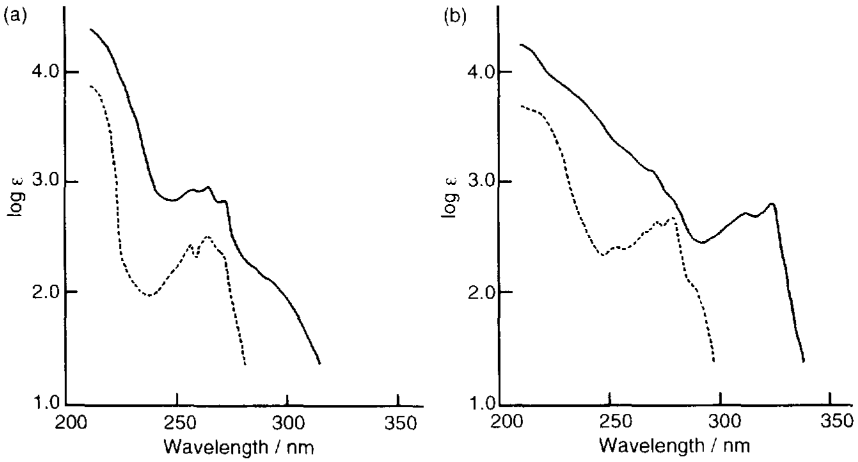


Fig. 1. Electronic spectra of (a) 1,2-paddlane **3** (solid line) and *o*-xylene (dotted line) and (b) 1,2,4,5-paddlane **11** (solid line) and durene (dotted line) in cyclohexane.

The structural features are also reflected in ^{1}H NMR spectroscopy. Table 1 lists the chemical shifts of the aromatic protons of paddlanes. As expected from the structure, **3** does not show any largely high-field-shifted aromatic protons, compared with other paddlanes. Three paddlanes **1c**, **2b**, and **11** have aromatic protons (H_a) surrounded by cyclobutane methylene groups. The aromatic protons not only suffer from the compression[18] caused by this situation and shift to the lower field, but also are affected by the benzene ring current and shift reversely to the higher field. These protons shift to the lower field by 0.6 to 0.7 ppm, relative to the corresponding reference cyclophanes, *syn*-[2.2]metacyclophane[19] for **1c**, $[2_3]$(1,3,5)cyclophane[20] for **2b**, and $[2_4]$(1,2,4,5)cyclophane[21] for **11**.

Table 1. ^1H NMR Spectroscopic Data of Aromatic Protons of Paddlanes

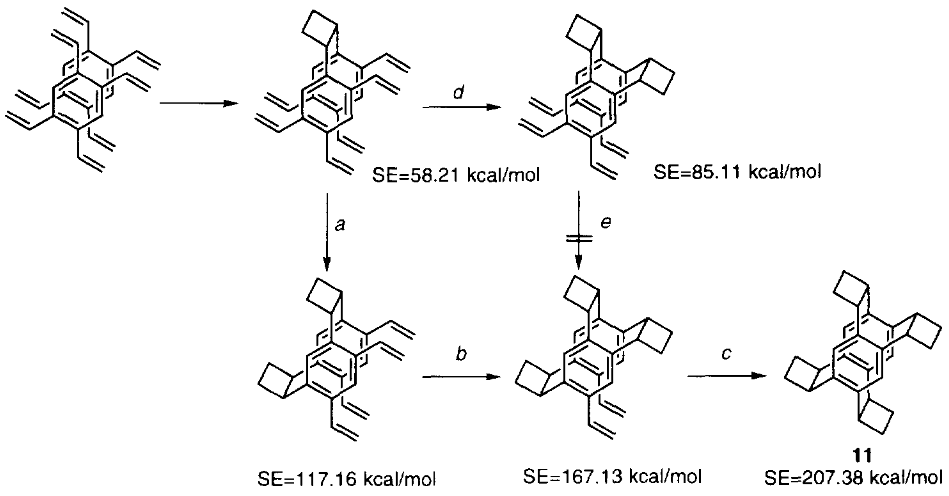
Paddlane	Chemical shift, δ				Ref.
	H_a	H_b	H_c	H_d	
1a	6.81 (2H, t, 7.7)	6.57 (4H, dd, 7.7, 1.7)	6.24 (2H, t, 1.7)		(4)
1b	6.68 (2H, s)	6.68 (2H, t, 7.4)	6.62 (2H, dt, 7.4, 1.5)	6.28 (2H, dt, 7.4, 1.5)	(4)
1c	7.18 (6.58)[a] (2H, t, 1.6)	6.53 (2H, dd, 8.3, 6.8)	6.33 (2H, dd, 6.8, 1.6) 6.32 (2H, dd, 8.3, 1.6)		(4), (19)
2a	5.67 (6H, s)				(5)
2b	6.28 (5.73)[a] (2H, s)	5.72 (2H, s)	5.23 (2H, s)		(5), (20)
3	7.01 (8H, s)				This work
11	6.69 (5.96)[a] (4H, s)				This work, (21)

[a] Values in parentheses refer to the chemical shifts of H_a protons of corresponding cyclophanes. See text for details.

We have already concluded that the photocycloaddition of styrene derivatives in benzene proceeds through the singlet excited states.[15] The formation of **1a**, **1b**, and **1c** was clearly explained by NEER.[4,7-10] The exclusive formation of **3** and **11** is also rationalized by this principle, because exo,exo-conformers depicted above are much more stable than the other conformers.

Highly strained 1,2,4,5-paddlane **11** (steric energy (SE) = 207 kcal/mol) was produced albeit in the meager yield, whereas the less-strained 1,4-paddlane was not. This fact is understood by the zipper effect; a strained molecule which cannot be obtained in one step may be accessible by dispersing the increase of strain in several steps. As shown in Scheme 1 with their steric energies, the first easy transformation into divinyl-1,2-paddlane is followed by the severe second transformation into vinyl-1,2,4-paddlane, so that the first transformation should be into divinyl-1,3-paddlane. The transformation into 1,3-paddlane must overcome 59 kcal/mol energy difference of formation, the second step into 1,2,4-paddlane 50 kcal/mol, and the last step into **11** 40 kcal/mol. This kind of photocycloaddition in solution is known to proceed, in case that the difference in formation energy between olefins and products is less than ca. 70 kcal/mol, according to many experimental results we have so far obtained.[22] Therefore, it is reasonable to consider that 1,2,4,5-tetravinylbenzene cyclized through the steps *a*, *b*, and *c* in Scheme 1.

In conclusion, the intermolecular photocycloaddition of multi-vinyl substituted benzenes has proved to be useful for the preparation of 1,2-, 1,3-, 1,3,5-, and 1,2,4,5-paddlanes, although it cannot be directly applied to the synthesis of 1,2,3,4,5- and 1,2,3,4,5,6-paddlanes (superpaddlane), because the exo,endo-divinyl situation turns to form the indane moiety efficiently through the intramolecular reaction, which was actually observed in the reaction of 1,2,3-trivinylbenzene. Search of a sophisticated transformation toward superpaddlane is now in progress and will be reported elsewhere.



Scheme 1. Possible cyclization path to paddlane **11**.

EXPERIMENTAL

Synthesis of 1,2-paddlane 3:

o-Divinylbenzene (85.1 mg, 0.65 mmol) in dry benzene (1 mL, 650 mM) was irradiated under a nitrogen atmosphere for 1 h with Pyrex-filtered light of a 400-W high-pressure mercury lamp. After evaporation of the solvent, the crude product was treated with a 1-M BH_3-THF solution (2 mL) and stirred for 12 h. Concentration of the mixture in vacuo left a residue, which was subjected to column chromatography (SiO_2, hexane) to afford 1,2-paddlane **3** in 11% yield (9.5 mg, 0.036 mmol) as a white solid.

Paddlane 3: M.p. 127.0–128.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.01 (8H, s, aromatic H), 4.00 (4H, m, methine H), 2.44 (8H, m, methylene H); ^{13}C NMR ($CDCl_3$) δ 139.7 (4C, aromatic C), 125.6 (4C, aromatic C), 124.6 (4C, aromatic C), 43.4 (4C, methine C), 22.5 (4C, methylene C); UV (cyclohexane) λ_{max} = 265 nm (ε = 890). Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.85; H, 7.72.

Photoirradiation of *p*-divinylbenzene:

Photoirradiation of *p*-divinylbenzene (77.7 mg, 0.597 mmol) in benzene (1 mL, 597 mM) for 1 h followed by column chromatography (SiO_2, hexane) afforded **5** in 28% yield as a colorless oil. This olefin (133.6 mg, 0.513 mmol) was further photoirradiated in benzene (200 mL, 2.6 mM), but no desired 1,4-paddlanes were detected.

***cis*-1,2-Bis(*p*-vinylphenyl)cyclobutane 5**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15 (4H, d, 8.3), 6.91 (4H, d, 8.3), 6.59 (2H, dd, 17.6 & 10.9), 5.61 (2H, d, 17.6), 5.10 (2H, d, 10.9), 4.04 (2H, m, methine H), 2.49 (4H, m, methylene H). HRMS (EI, 70 eV) m/z 260.1575, calcd for $C_{20}H_{20}$ 260.1565.

Photoirradiation of 1,2,3-trivinylbenzene:

2,6-Dibromophenyl triflate was prepared from 2,6-dibromophenol (10.6 g, 42.1 mmol) and triflic anhydride (13.2 g, 46.8 mmol) in pyridine (22 mL) in 76% yield. 1,2,3-Trivinylbenzene was prepared from 2,6-dibromophenyl triflate (2.55 g, 6.66 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol), tributylvinyltin (6.95 g, 21.9 mmol), *p-tert*-butylcatechol (a small amount), lithium chloride (0.85 g, 21.9 mmol) in dioxane (91 mL) with reflux for 4 h.[23] After column chromatography (SiO_2, hexane), 1,2,3-trivinylbenzene (365.2 mg, 2.34 mmol) was obtained in 35% yield as a colorless oil.

1,2,3-trivinylbenzene: ^1H NMR (200 MHz, $CDCl_3$) δ 7.38 (2H, d, 7.8), 7.16 (1H, t, 7.8), 6.91 (2H, dd, 17.3 & 11.0), 6.71 (1H, dd, 17.9 & 11.4), 5.57 (1H, dd, 11.4 & 2.0), 5.55 (2H, dd, 17.3 & 1.4), 5.21 (1H, dd, 17.9 & 2.0), 5.17 (2H, dd, 11.0 & 1.4). HRMS (EI, 70 eV) m/z 156.0946, calcd for $C_{12}H_{12}$ 156.0939.

Photoirradiation of 1,2,3-trivinylbenzene (78.0 mg, 0.50 mmol) in benzene (1 mL, 500 mM) for 50 min followed by column chromatography (SiO_2, hexane) afforded indane derivative **10** in 9% yield (7.0 mg) as a colorless oil. The desired 1,2,3-paddlane was not detected at all.

Intramolecular photoreaction product 10: ^1H NMR (200 MHz, $CDCl_3$) δ 7.28 (1H, m), 7.06 (2H, m), 7.00 (1H, dd, 17.7 & 11.0), 5.78 (1H, dd, 17.7 & 1.4), 5.31 (1H, dd, 11.0 & 1.4), 3.20 (1H, dd, 17.0 & 6.8), 2.93 (1H, d, 17.0), 2.46 (1H, m), 1.83 (1H, m), 1.11 (1H, m), 0.10 (1H, q, 4.0). HRMS (EI, 70 eV) m/z 156.0942, calcd for $C_{12}H_{12}$ 156.0939.

Synthesis of 1,2,4,5-Paddlane 11:

1,2,4,5-Tetravinylbenzene (104.3 mg, 0.572 mmol)[17] was irradiated in benzene (1 mL, 570 mM) for 25 min under conditions similar to those mentioned above to give **11** in 0.6% yield (0.64 mg, 0.17 mmol) as a white solid.

Paddlane 11: M.p. >300 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.69 (4H, s, aromatic H), 4.45 (8H, m, methine H), 2.58 (16H, m, methylene H); UV (cyclohexane) $\lambda_{max} = 324$ nm ($\varepsilon = 650$). HRMS (EI, 70 eV) m/z 364.2206, calcd for $C_{28}H_{28}$ 364.2190.

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