Notizen/Notes

1,2:9,10:16,17-Triethano[2$_3$](1,3,5)cyclophanes; Paddlanes with Cyclophane Shaft and Cyclobutane Blades[1]

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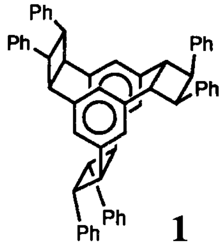
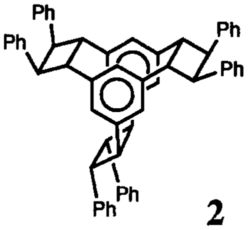
The symmetrical and unsymmetrical title compounds **3** and **4** were prepared by intermolecular photocycloaddition of 1,3,5-trivinylbenzene in 1% yield. The ratio of symmetrical and unsymmetrical paddlanes was 24:76, i.e. nearly a statistical one.

Hexaphenyl-substituted triethano[2$_3$](1,3,5)cyclophane (**1**), exhibiting C_3 symmetry, was synthesized by intermolecular photocycloaddition of 1,3,5-tristyrylbenzene and characterized by X-ray crystallographic analysis[2].



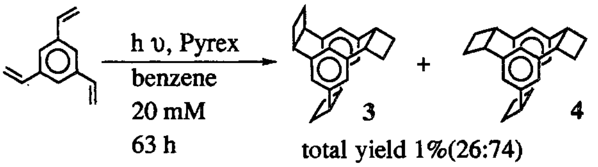
1



2

Compound **1**, a kind of paddlane, has attracted much attention[3]. In their first publication, the authors established the formation of the symmetrical paddlane **1** by this intermolecular photochemical reaction[2]; later on a second less symmetrical dimer was isolated in a ratio of 30:1[4]. The compound contains also three four-membered rings, thus structure **2** is the most plausible assumption. Since the products, fully substituted by phenyl groups, could not be easily analyzed by chromatographic or spectroscopic methods, especially by NMR spectroscopy, simple products of this family had to be synthesized in order to elucidate this kind of photoreaction as well as their spectroscopic properties.

Recently we have successfully synthesized the parent compounds **3** and **4** by intermolecular photocycloaddition of 1,3,5-trivinylbenzene. In the following we describe in detail their preparation and properties.



(1)

1,3,5-Trivinylbenzene (20 mM) was irradiated under nitrogen in benzene with Pyrex-filtered light of a mercury lamp for 63 h. The reaction mixture was concentrated and the residue treated with a diborane/THF solution[5], then purified by column chromatography (SiO$_2$, hexane/benzene). The fraction containing the tricyclized products was separated into the components **3** and **4** by HPLC. Both products are crystalline and showed melting points higher than 300°C. Mass spectroscopic analysis gave almost the same spectra for both compounds (see Experimental).

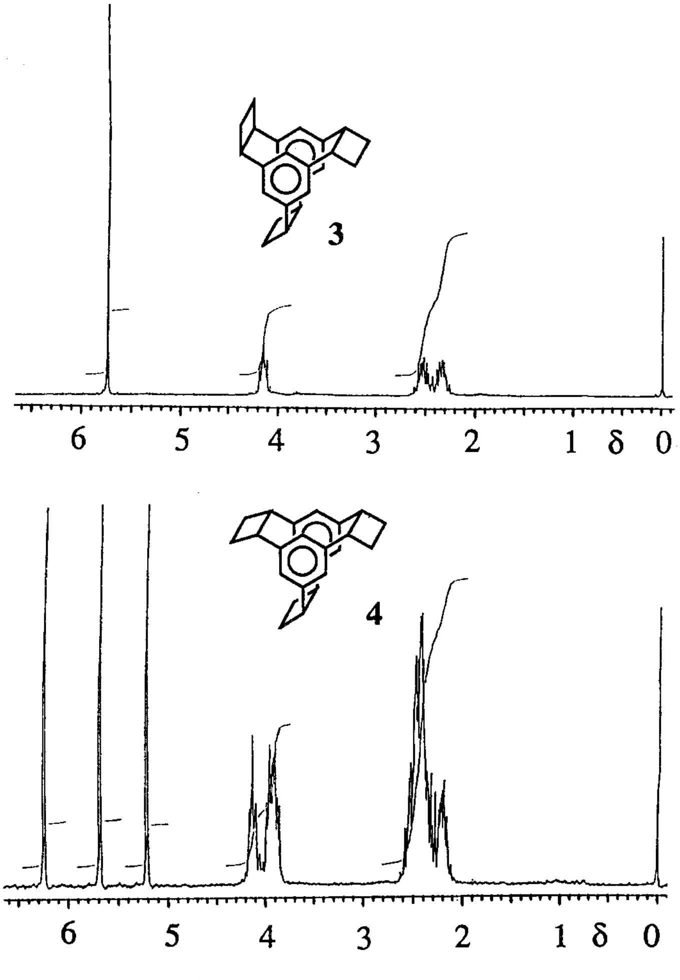


Figure 1. 200-MHz ^{1}H-NMR spectra of paddlanes **3** and **4** (CDCl$_3$)

The structures of products **3** and **4** were mainly determined by ^{1}H-NMR spectroscopy (Figure 1). The spectrum of **3** shows only one aromatic proton signal because of C_3 symmetry, whereas that of **4** reveals three singlets of aromatic protons due to the different magnetic environments. These aromatic signals are considerably shifted to higher field, due to the layered aromatic structures. Cyclobutane methine signals observed at around $\delta = 4$ also clearly reflect the symmetry modes of the molecules. The structure of the two products has further been supported by their ^{13}C-NMR spectra indicating only four signals for compound **3** (aromatic, $\delta = 144.5$ and 130.2; methine, 55.0; methylene 22.3) and 12 signals for compound **4** (aromatic, $\delta = 144.4$, 144.3, 144.2, 130.2, 129.8, and 129.5; methine, 55.0, 54.8, and 54.7; methylene, 22.3, 21.9, and 21.5).

The UV spectra of these paddlanes **3** and **4** are illustrated in Figure 2. Compared with 1,3,5-triethylbenzene, both show more broadened and bathochromically shifted bands than triethylbenzene. Hence the overlapped structures of **3** and **4** are proven.

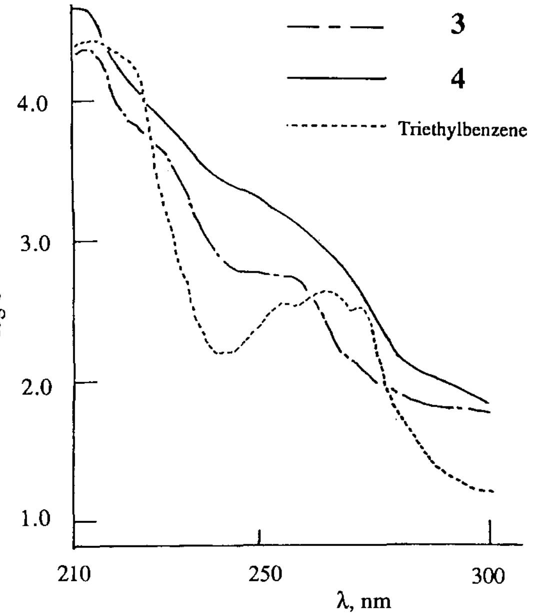
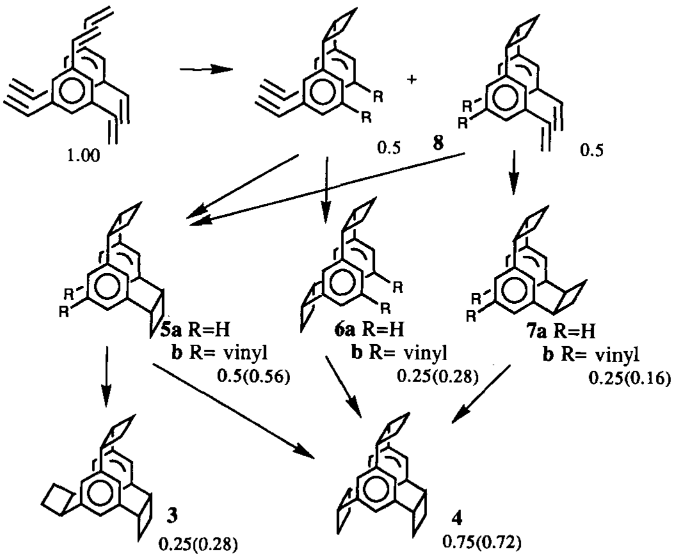


Figure 2. Ultraviolet absorption spectra of paddlanes **3** and **4** as well as 1,3,5-triethylbenzene measured in cyclohexane with a Shimadzu UV-160 spectrophotometer

The photoreaction was shown to involve stepwise formation of the products; first the amount of the monocyclized product increased with decreasing concentration of trivinylbenzene, then the amount of dicyclized products increased, while that of the monocyclized one remained nearly constant and decreased. The crude reaction mixtures always contained the products **3** and **4** in a ratio of ca. 1:3. The minor product displays C_3 symmetry. The product ratio is easily understood if the reaction takes place by random cyclization without any preference for the formation of rotamers resulting from rotation around vinyl groups (see Scheme 1). The MM2 calculation also supports the absence of energy differences between the rotamers of the divinyl intermediate **8**. In Scheme 1 the data abtained from the photocyclization of *m*-divinylbenzene are indicated in parentheses[6].

In order to improve the yield and product selectivity, 1,3,5-trivinylbenzene was irradiated in the presence of photosensitizers[7] such as benzophenone and *p*-dicyanobenzene and radical inhibitors such as catechol, hydroquinone, *p*-phenylphenol, *p*-*tert*-butylcatechol, *p*-quinone, and di-*tert*-butylhydroquinone. Moreover, materials such as cyclodextrins[8] serving as a receptor of two molecules were added to the reaction mixture. None of them, however, were so effective as to rise the yield or the selectivity.

Scheme 1



The present findings give an important guideline for the synthesis of parent paddlanes connected by cyclobutane rings[6], since the introduction of cyclobutane rings into tetramethylene bridges by any transannular reactions was found not to be promising[10].

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Experimental

Elemental analysis: Microanalytical Center of Gunma University. – NMR: Varian Gemini 200 FT NMR spectrometer, tetramethylsilane internal standard. – Reversed-phase HPLC: Shimadzu LC-6A HPLC apparatus. – Melting points are not corrected. – The MM2 program was provided by Prof. Dr. *E. Osawa* of Toyohashi University of Technology. – 1,3,5-Trivinylbenzene was prepared from 1,3,5-tris(1-hydroxyethyl)benzene according to the previously reported method[9]. Benzene was purified by distillation over sodium under nitrogen. The other materials and reagents were commercially available and used without further purification.

Preparation of Paddlanes **3** *and* **4**: 1,3,5-Trivinylbenzene (1.0 g, 6.4 mmol) in dry benzene (320 ml, 20 mM) was irradiated under nitrogen for 63 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[5] (2 ml) and stirred for 15 h. Concentration of the mixture in vacuo left a residue which was subjected to column chromatography (SiO_2, hexane) to afford a mixture of **3** and **4**; yield 10 mg (1%). The fraction containing tricyclized products was separated into the components **3** and **4** by HPLC (Shimapack®-C18, MeOH).

$C_{24}H_{24}$ (312.5) Calcd. C 92.26 H 7.74 Found C 92.25 H 7.75

Cyclophane **3**: m.p. >300°C. – MS: *m/z* (%) = 156 (100), 230 (2.2), 255 (2.1), 312 (3.4) [M^+]. – ^{1}H NMR ($CDCl_3$): $\delta = 5.67$ (s, 6H, aromatic H), 4.09 (m, 6H, methine H), 2.1–2.55 (m, 12H, methylene H). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 144.5$ (6 C, quart.

C), 130.2 (6 C, aromatic CH), 55.0 (6 C, methine C), 22.3 (6 C, methylene C).

Cyclophane **4**: m.p. >300°C. – MS: m/z (%) = 156 (100), 230 (2.4), 255 (2.2), 312 (5.8) [M$^+$]. – ^{1}H NMR (CDCl$_3$): δ = 6.28 (s, 2H, aromatic H), 5.72 (s, 2H, aromatic H), 5.23 (s, 2H, aromatic H), 4.16 (m, 2H, methine H), 4.00 (m, 4H, methine H), 2.3–2.6 (m, 10H, methylene H), 2.15–2.3 (m, 2H, methylene H). – ^{13}C NMR (CDCl$_3$): δ = 144.4 (2 C, aromatic quart. C), 144.3 (2 C, aromatic quart. C), 144.2 (2 C, aromatic quart. C), 130.2 (2 C, aromatic C), 129.8 (2 C, aromatic C), 129.5 (2 C, aromatic C), 55.0 (2 C, methine C), 54.8 (2 C methine C), 54.7 (2 C methine C), 22.3 (2 C, methylene C), 21.9 (2 C, methylene C), 21.5 (2 C, methylene C).

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[1] Intramolecular [2 + 2] Photocycloaddition, 16. – For Part 15 see ref.[9].

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[133/92]

CAS Registry Numbers

3: 141902-97-8 / **4**: 141902-98-9 / Trivinylbenzene: 3048-52-0