Pergamon

Tetrahedron Letters, Vol. 38, No. 11, pp. 1983-1986, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00254-2

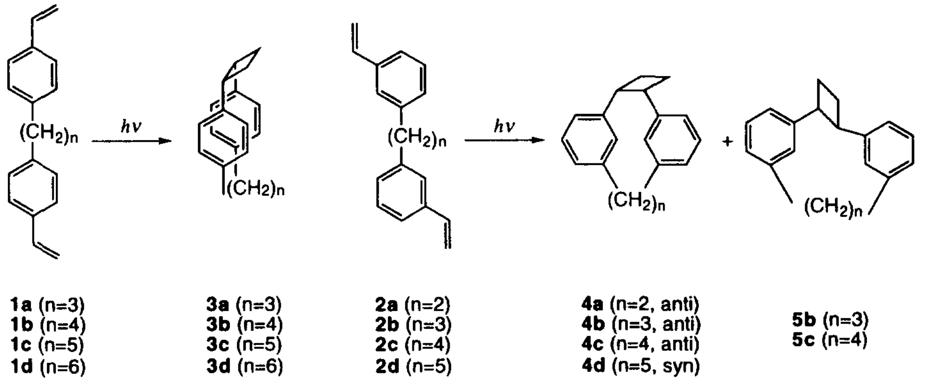
Synthesis of 1,8-Naphthylene-Bridged *syn*-Cyclophanes by Efficient Intramolecular [2 + 2] Photocycloaddition

Yosuke Nakamura, Miho Matsumoto, Yoshitou Hayashida, and Jun Nishimura*

Department of Chemistry, Gunma University, Tenjin-cho, Kiryu, Gunma 376, Japan

Abstract: Novel 1,8-naphthylene-bridged para- and metacyclophanes were efficiently synthesized as a single isomer by the intramolecular [2 + 2] photocycloaddition of 1,8-bis(*p*- and *m*-vinylphenyl)-naphthalenes, respectively. By this method, *syn*-cyclophanes were selectively obtained in both cases.

We have reported that the intramolecular [2 + 2] photocycloaddition of α,ω-bis(vinylphenyl)alkanes **1** and **2** readily afforded [2.n]para- and metacyclophanes (**3**–**5**) having a cyclobutane ring (Scheme 1).[1] Paracyclophanes **3** obtained from **1** were found to be exclusively of syn-configuration, possessing a *cis*-disubstituted cyclobutane ring, although the yields were sensitively influenced by the length of the oligomethylene chain. On the other hand, the stereochemistry of the metacyclophanes obtained from **2** depended on the chain length. For example, **2a** (n=2) afforded only **4a** in an anti-form with a *cis*-disubstituted cyclobutane ring, whereas **2b** (n=3) afforded not only **4b** but also **5b** with a *trans*-disubstituted cyclobutane ring. Only **2d** (n=5) afforded *syn*-cyclophane **4d**. The variety in the stereochemistry of the products is mainly ascribed to the flexibility of the oligomethylene chain connecting the two styrene moieties.

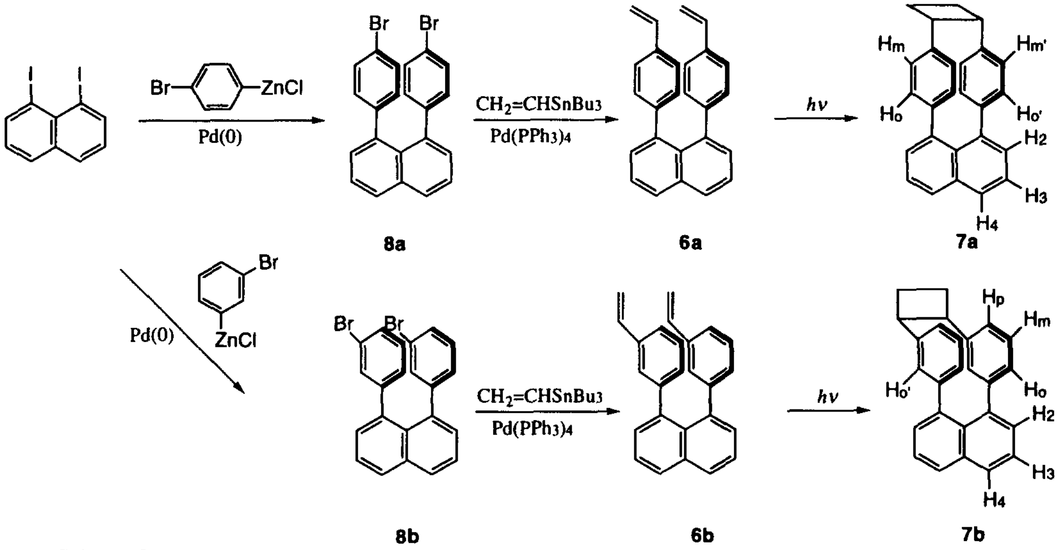


Scheme 1.

In this study, aiming at the selective synthesis of *syn*-cyclophanes, we have utilized a rigid 1,8-naphthylene as a bridging unit, and examined the photoreaction of 1,8-bis(vinylphenyl)naphthalenes **6a** and **6b**.

In these compounds, the two styrene moieties are expected to be arranged approximately perpendicular to the naphthalene ring and almost in parallel to each other. Although the two benzene rings slightly deviate outside,[2] the distances between the two vinyl groups in **6a** and **6b** are estimated as ca. 3.5 Å, according to the MM2 calculations. Therefore, the intramolecular photocycloadditon of **6a** and **6b** is expected to proceed smoothly, unless the 1,8-naphthylene unit influences the relaxation process of the excited state of the styrene moieties and prevents the [2 + 2] photocycloaddition. The intramolecular photocycloadditon of **6a** and **6b** should give exclusively cyclophane **7a** and *syn*-cyclophane **7b** with a *cis*-disubstituted cyclobutane ring; the formation of *anti*-cyclophanes or cyclophanes with a *trans*-disubstituted cyclobutane ring seems to be unlikely due to the steric reasons. In practice, **6a** and **6b** successfully afforded *syn*-cyclophanes **7a** and **7b**, respectively. These cyclophanes are also of great interest from the viewpoint of the interaction between the two benzene rings and the bridging 1,8-naphthylene unit.

The synthetic routes of **6a** and **6b** are shown in Scheme 2. 1,8-Bis(bromophenyl)naphthalenes **8a** and **8b** were synthesized by the palladium-catalyzed coupling reaction of 1,8-diiodonaphthalene with *p*- and *m*-bromophenylzinc chloride prepared from bromophenyllithium and zinc chloride in situ.[3] Bromides **8a** and **8b** were allowed to react with tributylvinyltin again in the presence of palladium catalysis,[4] readily affording **6a** and **6b**, respectively. Bis(*m*-substituted phenyl)naphthalenes **6b** and **8b** were obtained as a mixture of syn- and anti-conformers in contrast with **6a** and **8a** consisting of a single conformer, and their separation was unsuccessful due to the fast interconversion between them at room temperature, as suggested by House et al. previously.[2,5] Thus, **6b** and **8b** afforded quite broadened peaks in their ^1H NMR spectra, especially in the region of the benzene rings.

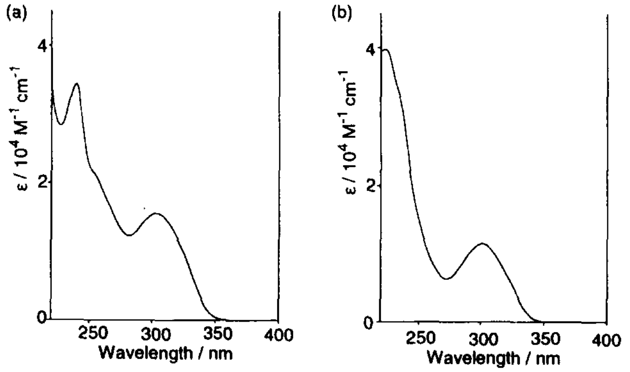


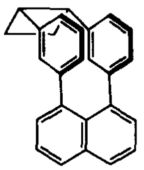
Scheme 2.

The intramolecular [2 + 2] photocycloaddition of **6a** and **6b** was carried out in benzene (ca. 2 mM) with a 400-W high-pressure mercury lamp through a Pyrex filter in a manner similar to that reported previously.[1] During 30 min-irradiation, **6a** and **6b** were almost completely consumed, leading to the corresponding cyclophanes **7a** and **7b** as a single product in excellent 90 and 85% yield, respectively. The photoreaction of **6b** was slightly slower than that of **6a**, probably because the relative arrangement of the two vinyl groups in **6b** continuously varies due to the rotation of the benzene rings, whereas that in **6a** is almost independent of the rotation.

The structure of **7a** and **7b** was characterized by NMR and mass spectroscopies.[6] The benzene protons of **7a** and **7b** were apparently high-field-shifted relative to those of **6a** and **6b**, respectively. The shift in **7a** (0.2–0.6 ppm) is more remarkable than in **7b** (0.1–0.3 ppm), indicating that the two benzene rings in **7a** are brought closer together by the cyclobutane ring and suffer from more shielding effects. This result is compatible with the fact that the two benzene rings of 1,8-diarylnaphthalenes slightly deviate outside.[2] Since the two vinyl groups in the meta-positions can be slightly closer to each other than those in the para-positions, the arrangement of the two benzene rings seems to be relatively unchanged during the cycloaddition of **6b**. The unequivalence of the four benzene protons in **7a** obviously indicates that the rotation of the benzene rings is prevented by the cyclobutane ring and its direction is also fixed to one side. The protons of the benzene rings in **7b** were observed as sharp peaks in contrast with those in **6b**, because of the restriction of the rotation of the benzene rings.

The formation of only one product **7b** is noticeable. There seem to be two possible isomers (**7b** and **7b'**) from the photocycloaddition of **6b**, since the vinyl groups of **6b** are virtually free to rotate. Actually, in other similar cases,[1,7] two or more isomers derived from the difference in the configuration of the cyclobutane ring were obtained. The structure of **7b** is supported by its ^{1}H NMR spectrum, where the four methylene protons of the cyclobutane rings are resonated at similar fields; in the case of **7b'**, the two protons among the four should be rather high-field-shifted due to the shielding effect of the naphthalene nucleus. In the NOESY experiments, NOE interaction was detected between the cyclobutane methylene protons and the H_p protons in the benzene rings (see structure **7b**). Furthermore, the consideration of the conformation of the vinyl groups in **6b** suggests the formation of **7b** rather than **7b'**. The two vinyl groups are expected to be predominantly directed to exo rather than endo in the ground state, due to the steric hindrance with the opposite benzene ring during the rotation of the benzene rings.





7b'

Fig. 1. Absorption spectra of (a) **6a** and (b) **7a** in cyclohexane at room temperature.

The absorption spectra of **6a** and **7a** in cyclohexane are shown in Figure 1. The spectrum of **6a** is quite similar to that of 1,8-diphenylnaphthalene in the literature.[8] The band in the region of more than 300 nm, which is absent in naphthalene itself, is ascribed to the electronic interaction between the naphthalene and benzene rings. The electronic properties of 1,8-diphenylnaphthalene are little affected by the two vinyl groups. In **7a**, however, the band around 300 nm is somewhat weakened, and the strong absorption band at shorter wavelengths (224 nm) is blue-shifted relative to **6a** (239 nm). These observations are apparently derived from the decrease in the coplanarity between the naphthalene and two benzene rings due to the bridging by the cyclobutane ring.

In conclusion, novel 1,8-naphthylene-bridged paracyclophane **7a** and *syn*-metacyclophane **7b** were efficiently and selectively obtained as a single isomer by the intramolecular [2 + 2] photocycloaddition of **6a** and **6b**, respectively. The bridging by a 1,8-naphthylene unit is apparently favorable for the photocycloaddition of the two styrene moieties on the steric aspects, without disturbing it on the electronic aspects. Therefore, this method seems to be widely applicable to the synthesis of other cyclophanes such as naphthalenophanes, phenanthrenophanes, and pyrenophanes whose physicochemical properties are of more interest.

Acknowledgment: This work was supported by the Nishida Research Fund for Fundamental Organic Chemistry and the Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan.

REFERENCES AND NOTES

1. Nishimura, J.; Doi, H.; Ueda, E.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, 109, 5293; Nishimura, J.; Ohbayashi, A.; Doi, H.; Nishimura, K.; Oku, A. *Chem. Ber.* **1988**, 121, 2019.
2. House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, 37, 1003.
3. Negishi. E; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, 42, 1821.
4. Kosugi, M.; Sasazawa, K.; Shimizu, Y.; Migita, T. *Chem. Lett.* **1977**, 301; McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422; Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
5. House, H. O.; Campbell, W. J.; Gall, M. *J. Org. Chem.* **1970**, 35, 1815.
6. The spectral data of **7a** and **7b** are as follows. **7a**: mp. 226–227 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (2H, dd, J = 7.9 & 1.2 Hz, H_4), 7.62 (2H, 2H, dd, J = 7.4 & 1.2 Hz, H_2), 7.55 (2H, dd, J = 7.9 & 7.4 Hz, H_3), 6.70 (4H, s), 6.55 (2H, d, J = 7.6 Hz), 6.30 (2H, d, J = 7.6 Hz), 4.3 (2H, m), 2.6 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.76, 140.30, 139.56, 135.90, 132.39, 130.69, 130.30, 130.24, 128.89, 128.85, 126.99, 124.80, 48.31, 19.98; HRMS m/z 332.1592, calcd for $C_{26}H_{20}$ 332.1565. **7b**: mp. 147–148 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (2H, dd, J = 8.2 & 1.2 Hz, H_4), 7.48 (2H, 2H, dd, J = 8.2 & 7.0 Hz, H_3), 7.34 (2H, dd, J = 7.0 & 1.2 Hz, H_2), 6.89 (2H, t, J = 7.6 Hz, H_m), 6.74 (2H, d, J = 7.6 Hz, H_o), 6.72 (2H, s, $H_{o'}$), 6.68 (2H, d, J = 7.6 Hz, H_p), 4.2 (2H, m), 2.5 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.88, 140.67, 139.28, 135.72, 135.16, 130.47, 129.55, 129.04, 127.81, 125.87, 124.54, 123.80, 47.07, 20.36; HRMS m/z 332.1540, calcd for $C_{26}H_{20}$ 332.1565.
7. Nishimura, J.; Takeuchi, M.; Takahashi, H.; Ueda, E.; Wada, Y.; Oku, A. *Bull. Chem. Soc. Jpn.* **1989**, 62, 3161; Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. *J. Am. Chem. Soc.* **1991**, 113, 3485; Wada, Y.; Ishimura, T.; Nishimura, J. *Chem. Ber.* **1992**, 125, 2155; Takeuchi, M.; Tuihiji, T.; Nishimura, J. *J. Org. Chem.* **1993**, 58, 7388; Nakamura, Y.; Tshuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Am. Chem. Soc.* **1996**, 118, 1006.
8. House, H. O.; Magin, R. W.; Thompson, H. W. *J. Org. Chem.* **1963**, 28, 2403.

(*Received in Japan* 13 *January* 1997; *revised* 3 *February* 1997; *accepted* 7 *February* 1997)