Pergamon

Tetrahedron Letters 40 (1999) 6781–6784

TETRAHEDRON
LETTERS

Photolysis of $[3_4](1,2,3,5)$cyclophane: formation of a pentacyclo$[6.3.1.1^{6,10}.0^{3,7}.0^{4,10}]$dodecane skeleton with abnormally elongated C–C single bonds[1]

Chultack Lim,[a] Mikio Yasutake[a,b] and Teruo Shinmyozu[a,*]

[a] *Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University, Hakozaki, Fukuoka 812-8581, Japan*
[b] *Department of Chemistry, Graduate School of Science, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan*

Received 6 May 1999; revised 23 June 1999; accepted 25 June 1999

Abstract

The photolysis of $[3_4](1,2,3,5)$cyclophane **5** in H_2O-saturated CH_2Cl_2 produced the novel polycyclic caged diol **6** with a pentacyclo$[6.3.1.1^{6,10}.0^{3,7}.0^{4,10}]$dodecane skeleton **4**, which has abnormally elongated C–C single bonds (1.624 Å). The structural features of **6** were studied using the X-ray structural analysis and ab initio MO calculations. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: hexaprismane; photolysis; cyclophane; polycyclic caged compound.

Our recent interest has focused on the challenging objective of synthesizing hexaprismane **1**[2] and its derivatives, therefore, we have studied the photolysis[3,4] of multibridged $[3_n]$cyclophanes.[5] Previously, we reported that the photolysis of $[3_4](1,2,4,5)$cyclophane **2**[6] afforded a new polycyclic caged diol **3** with a novel pentacyclo$[6.3.1.1^{6,10}.0^{3,7}.0^{4,10}]$dodecane skeleton **4**.[4] For the formation of **3**, we proposed a series of reactions involving the initial formation of a hexaprismane derivative **7** followed by the protonation and equilibration of the resultant carbocations, and interception of the most stable cation with a hydroxide ion.[3,4] We now describe the structural features of the photoproduct of $[3_4](1,2,3,5)$cyclophane **5**,[5] which has a different substitution pattern of four trimethylene bridges from that of **2**.

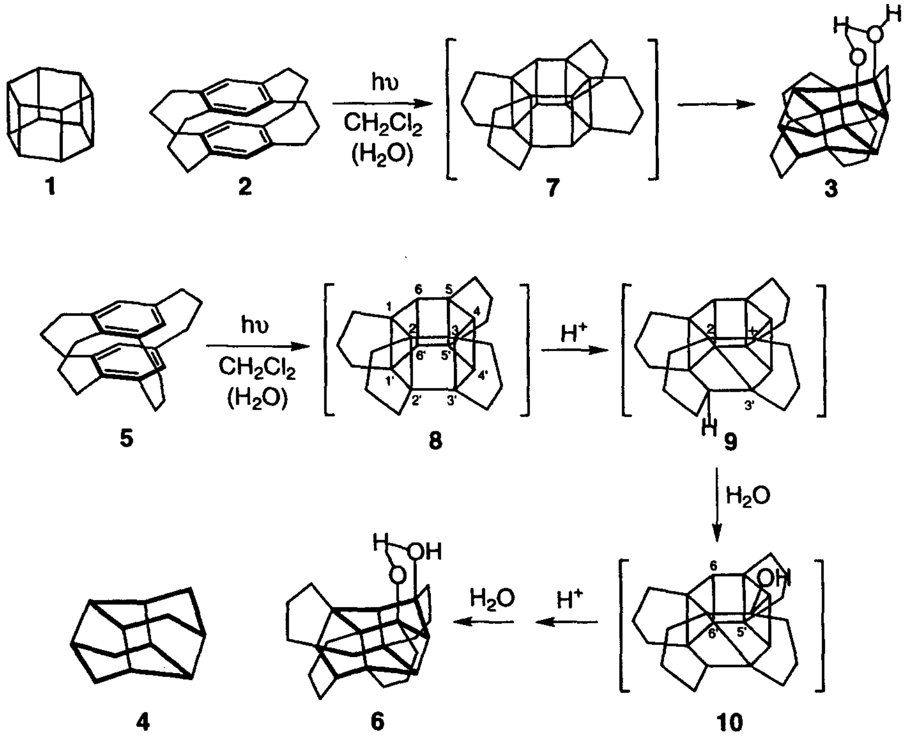
A H_2O-saturated CH_2Cl_2 solution (3.8×10^{-3} mol/L) of **5** was irradiated with a low pressure Hg lamp for 3 h at room temperature under Ar. Separation of the reaction mixture by silica gel column chromatography with AcOEt:hexane (1:5) gave the starting **5** (40%) and new caged diol **6**[7] as colorless crystals (4.5%) (Scheme 1). The X-ray structural analysis showed the new polycyclic caged structure for **6**, which is composed of five chair-cyclohexanes and five cyclopentanes.[8] Three of the chair-cyclohexanes are transformed from the original trimethylene bridges and the remaining two originate from the benzene rings. The molecular structure of **6** is similar to that of **3**, but the latter is composed of six chair-cyclohexanes and four cyclopentanes. Although the skeleton **4** of **6** is the same as that of **3**, the C3–C10

---

[*] Corresponding author. Fax: +81-92-642-2735; e-mail: shinmyo@ms.ifoc.kyushu-u.ac.jp

PII: S0040-4039(99)01275-7

and C6–C7 bond lengths, which are connected to the upper and lower chair-cyclohexanes, are abnormally long [both 1.624(4) Å] as compared with the C–C bond length of cyclopentane (1.552 Å) optimized by the RHF/6-31G* basis set,[9] and even with the corresponding bond lengths [1.603(4) and 1.610(4) Å] of **3** (Fig. 1). All four trimethylene bridges of **2** are transformed into the chair-cyclohexanes in **3**, whereas the trimethylene bridge of **5** is converted into a cyclopentane ring involving the C3 and C10 bridgeheads. As a result, **6** is less stable than **3** by 6.8 kcal mol^{-1} based on the ab initio MO calculations (RHF/6-31G*) mainly due to the presence of a more strained cyclopentane ring (ca. 6 kcal mol^{-1}) in place of a cyclohexane ring.[9] The upper and lower six-membered rings of **6** are distorted chair-cyclohexanes; the dihedral angles of the C1–C2–C4–C5 and C5–C6–C1 planes (105.3°) as well as the C8–C9–C11–C12 and C9–C10–C11 planes (103.6°) are much smaller than those of the C1–C2–C4–C5 and C2–C3–C4 planes (151.1°) and C8–C9–C11–C12 and C8–C7–C12 planes (155.6°), respectively. The corresponding value of a chair-cyclohexane estimated by the RHF/6-31G* level MO calculations is 130.5°. Both cyclohexane rings of **6** are slightly more deformed than those of **3**.



Scheme 1. Photochemical reactions of **2** and **5**

The formation of **6** may be explained by the protonation of the most strained C2–C2′ bond of **8**, followed by formation of the C2–C3′ bond giving the cation **9**, which is intercepted by water to afford **10**. Further protonation of the C6′ carbon and subsequent formation of the C6–C5′ bond and interception of the resulting carbocation by water may provide **6**. Further application of this photolysis to the higher homologues of **5**, elaboration of the reaction mechanisms, and our effort toward the isolation of the hexaprismane derivatives are currently under intense investigation.

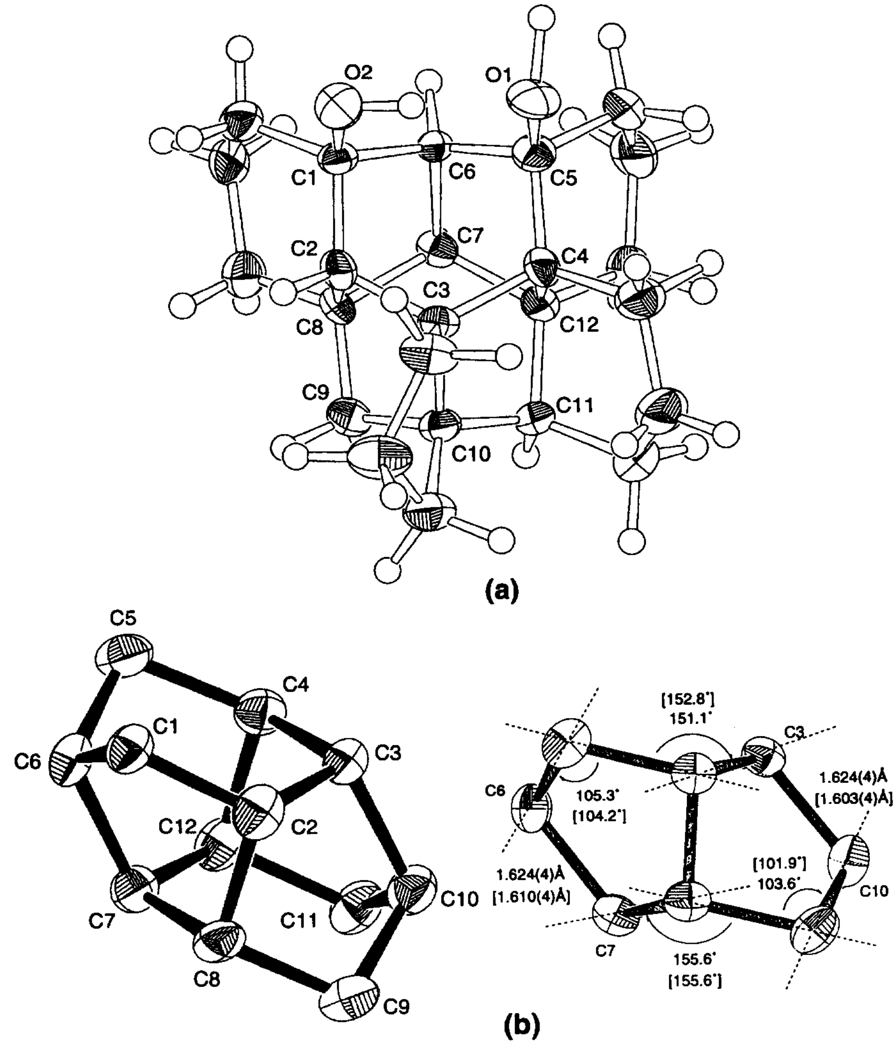


Figure 1. (a) ORTEP drawing of **6** (50% probability ellipsoids). (b) Crystal structure of the skeleton of **6** (hydrogen atoms are omitted for clarity). Values in brackets are those of the corresponding skeleton of **3**

Acknowledgements

We gratefully acknowledge the financial support by a Grant-in-Aid for the Priority Area (A) of Creation of Delocalized Electronic Systems (no. 11133244) and Scientific Research (B) (no. 09440221) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. Multibridged [3$_n$]Cyclophanes, 9.
2. For recent reviews, see: (a) Dodziuk, H. In *Topics in Stereochemistry*, Vol. 21; Eliel, E. L.; Wilen, S. H., Eds.; John Wiley & Sons, 1994. (b) Forman, M. A. *Org. Prep. Proced. Int.* **1994**, *26*, 291–320.
3. Sakamoto, Y.; Kumagai, T.; Matohara, K.; Lim, C.; Shinmyozu, T. *Tetrahedron Lett.* **1999**, *40*, 919–922.
4. Lim, C.; Yasutake, M.; Shinmyozu, T. submitted to *Angew. Chem., Int. Ed. Engl.* (Multibridged [3$_n$]Cyclophanes, 8).

5. (a) Sakamoto, Y.; Miyoshi, N.; Hirakida, M.; Kusumoto, S.; Kawase, H.; Rudzinsky, J. M.; Shinmyozu, T. *J. Am. Chem. Soc.* **1996**, *118*, 12267–12275. (b) Sakamoto, Y.; Shinmyozu, T. *Recent Res. Devel. in Pure & Applied Chem.* **1998**, 2, 371–399.
6. Sentou, W.; Satou, T.; Yasutake, M.; Lim, C.; Shinmyozu, T. *Eur. J. Org. Chem.* **1999**, 1223–1231.
7. Selected spectroscopic data and elemental analysis for **6**: mp 270–271°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04–2.03 (m, 30H), 4.46 (S, 2H, -OH); ^{13}C NMR (150MHz, $CDCl_3$, DEPT) δ 16.0 (sec.), 19.0 (sec.), 19.7 (sec.), 20.3 (sec.), 22.5 (sec.), 27.2 (sec.), 28.6 (sec.), 29.0 (sec.), 29.3 (sec.), 34.6 (sec.), 36.3 (sec.), 40.7 (sec.), 49.9 (tert.), 50.7 (quat.), 54.1 (tert.), 54.6 (quat.), 55.4 (quat.), 55.5 (sec.), 55.7 (tert.), 58.2 (quat.), 68.0 (tert.), 71.5 (quat.), 83.0 (quat.), 85.9 ppm (quat.). FABMS: *m/z* 352 (M^+). Anal. calcd for $C_{24}H_{32}O_2 \cdot 1/2H_2O$: C, 79.74%; H, 9.20%. Found: C, 79.34%; H, 8.85%.
8. Crystal Data for **6**: $C_{24}H_{32}O_2$, *Mr*=352.52, monoclinic spece group *P21/c* (#14), *a*=9.20 2 (10), *b*=13.658(4), *c*=14.455(4) Å, β=95.946(4)°, *Z*=4, *V*=1806.86 Å^3, μ_{Mo}=0.80 cm^{-1} (Rigaku RAXIS-IV imaging plate), 2321 reflections with *I*>3.00(I), *R* (Rw)=0.046 (0.032). Crystallographic data (excluding structure factor) for structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication no. CCDC-119350. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-33603; e-mail: deposit@ccdc.cam.ac.uk).
9. The computations were performed with ab initio MO calculations, and the Gaussian 94 program (see: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh PA, 1995) graphically facilitated by Insight II from Ryoka Systems, Inc., on Silicon Graphics Octane, was used.