Pergamon

Tetrahedron Letters 40 (1999) 919–922

TETRAHEDRON
LETTERS

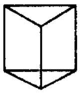
Formation of Novel Cage Compounds via Photoreaction of [3.3.3](1,3,5)Cyclophane[1]

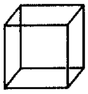
Youichi Sakamoto,[a,b] Tsutomu Kumagai,[c] Kumi Matohara,[a,b] Chultack Lim,[a]
and Teruo Shinmyozu[a,*]

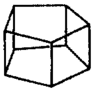
[a]Institute for Fundamental Research of Organic Chemistry (IFOC) and [b]Department of Chemistry, Graduate School of Science,
Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan.
[c]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8577, Japan

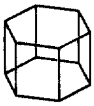
Received 25 March 1998; revised 19 November 1998; accepted 20 November 1998

Abstract: Photoirradiation of $[3_3]$(1,3,5)cyclophane **11** with a low pressure Hg lamp in CH_2Cl_2 in the presence or absence of water afforded new polycyclic cage compounds of chlorinated tribridged hexacyclododecane **12** or its hydroxy analogue **14** and tribridged tetracyclic olefin **13**. © 1999 Elsevier Science Ltd. All rights reserved.


1

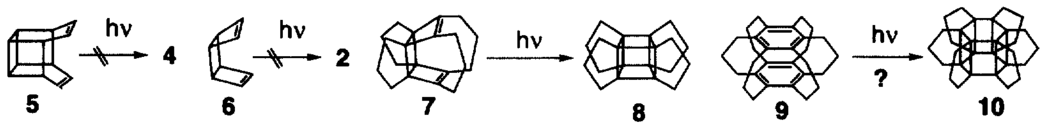

2


3

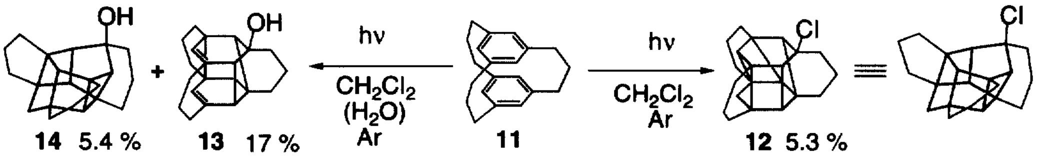

4

Prismanes constitute a fascinating family of $(CH)_n$ polyhedra,[2] several members of which, namely prismane **1**,[3] cubane **2**,[4] and pentaprismane **3**[5] have been successfully synthesized. Recently, attention has focused on the challenging objective of synthesizing the higher prismanes, in particular, hexaprismane **4**. Despite much effort, **4** has eluded synthesis so far.[6-8] For example, pentacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{6,9}]dodeca-4,10-diene **5**, an attractive and seemingly appropriate precursor, did not isomerized to **4**.[9] Similarly *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene **6** did not isomerize to cubane **2**. However, the device of attaching trimethylene bridges to the basic skeleton makes the reaction allowed, aptly demonstrated by the photochemical synthesis of propella$[3_4]$prismane **8** from diene **7**.[10] These findings have been rationalized in terms of the order of the frontier molecular orbitals which are largely affected by through-bond interactions.[11-14] Based on Frontier MO consideration, Osawa et al. predicted that [3]superphane **9**[15] on irradiation might be isomerized to hexaprismane derivative **10** (Scheme 1).[11] We decided to approach the construction of the hexaprismane skeleton in a different way by irradiating multibridged $[3_n]$cyclophanes. We planned to optimize reaction conditions first by using $[3_3]$(1,3,5)cyclophane **11**,[16] which is the lower homologue of **9** and available in large quantity, and then apply the conditions to [3]superphane **9**. We now describe formation and characterization of three novel polycyclic hydrocarbons **12**, **13**, and **14** which are obtained from **11** (Scheme 2).

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)02489-7



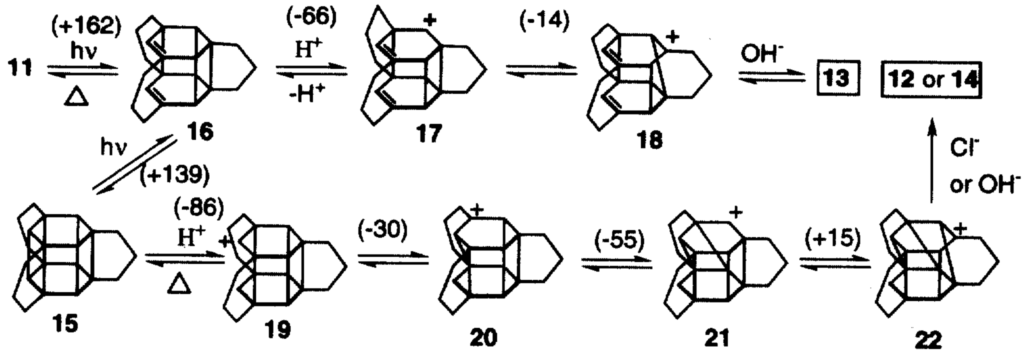
Schceme 1. Forbidden photochemical reactions of **5** to **4** and **6** to **2**, Gleiter's photochemical synthesis of **8** from **7**, and expected photochemical isomerization of **9** to **10**.



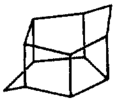
Scheme 2. Photochemical reactions of **11** in dry CH_2Cl_2 or CH_2Cl_2 containing H_2O under irradiation of a low pressure Hg lamp.

Irradiation of **11** with a low pressure mercury lamp in cyclohexane, methanol, or benzene left **11** intact, but caused some of the usual polymerization. However, in CH_2Cl_2 two types of products were formed. A solution of **11** in dry CH_2Cl_2 (4.90×10^{-3} mol/L) was irradiated for 2.5 h at room temperature under Ar. Separation of the reaction mixture by column chromatography (SiO_2, hexane) afforded **11** (40 %) and new cage compound, the bridged hexacyclic chlorododecane **12** (5.3 %).[17] The structure of **12** was identified from its molecular formula, $C_{21}H_{25}Cl$ and NMR spectra. The proton decoupled ^{13}C NMR spectrum shows ten signals for the secondary carbon, five for the tertiary carbon, and six for the quaternary carbon atoms on the basis of the distortionless enhancement by polarization transfer (DEPT) spectrum. The ^1H-^{13}C correlation spectroscopy indicated two types of adjacent tertiary carbon (R_2CH-CHR_2; R = quaternary carbon atoms) and three types of tertiary carbon atoms surrounded by three quaternary carbon atoms (R_3CH; R = quaternary carbon atoms).

Similarly irradiation of **11** in a water-saturated CH_2Cl_2 solution (1.45×10^{-2} mol/L) for 2.5 h under Ar, followed by separation by column chromatography (SiO_2, hexane:AcOEt, 10:1) gave **11** (18 %) and two photoproducts; the polycyclic olefin **13** (17 %)[18] and the cage compound **14** (5.4%),[19] a hydroxy analogue of **12**. Of the twenty-one signals of the proton decoupled ^{13}C NMR spectrum of **13**, six, five, and ten signals are assigned to quaternary, tertiary, and secondary carbon atoms based on the DEPT spectrum. The product **13** contains two different double bonds (R_2C=CHR) since the signals at 136.0, 139.3, 141.3, and 144.1 ppm are assigned to *sp2* carbons. The ^1H-^{13}C correlation spectroscopy indicates two types of adjacent tertiary carbon atoms (R_2CH-CHR_2; R = quaternary carbon atoms) and a tertiary carbon atoms surrounded by three quaternary carbon atoms (R_3CH). The ^1H and ^{13}C NMR spectra of **14** are quite similar to those of **12**, suggesting the similar molecular geometries.



Scheme 3. Expected mechanism for the formation of **12**, **13**, and **14**. The values (kcal/mol) denote the gain or release of steric energies estimated by MM3.



23

It is likely that **11** on irradiation in CH_2Cl_2 gives the hexaprismane **15** and its diene precursor **16** as the primary photoproducts. However, they could not be isolated presumably owing to their highly strained nature and reversion to **11**. The formation of **11** was confirmed by the ^{1}H NMR spectrum when the olefin **13** was irradiated under similar conditions. In wet CH_2Cl_2, the protonation of **15** and **16** occurs. The resulting cations **19** and **17** then equilibrate to their more stable isomers **18**-**22**. Finally, **22** and **18** are intercepted by chloride and hydroxide ions to give products **12**, **13**, and **14**. The driving force of the formation of **13** or **12** and **14** may be ascribed to the release of the molecular strain of **15** or **16** (Scheme 3). The values (kcal/mol) in the parenthesis indicate the gain or release of the steric energies estimated by MM3(92) in the reaction.[20] This study demonstrated that the irradiation of **11** in CH_2Cl_2 gave the cage compounds **12** and **14** having a dihomopentaprismane skeleton **23**. Further investigation of the reaction mechanism as well as photochemical reactions of higher homologues of **11** including [3]superphane **9** are in progress.

We gratefully acknowledge financial support by the Grant-in-Aid for the Priority Area (A) of Creation of Delocalized Electronic Systems (no. 10146237) and Scientific Research (B) (no. 09440221) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes:

*E-mail: shinmyo@ms.ifoc.kyushu-u.ac.jp

1. Multibridged [3_n]Cyclophanes, 6.
2. For recent reviews, see. (a) Dodziuk, H. In 'Topics in Stereochemistry, Vol. 21", Eliel, E. L.; Wilen, S. H. (Eds), John Wiley & Sons, Inc., 1994. (b) Forman, M. A. *Org. Prep. Proced. Int.*, **1994**, 26, 291.
3. Katz, T. J.; Acton, N. *J. Am. Chem. Soc.*, **1973**, 86, 3157.
4. Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.*, **1964**, 103, 2134.

5. Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.*, **1981**, 103, 2134.
6. Eaton, P. E.; Chakraborty, U. R. *J. Am. Chem. Soc.*, **1978**, 100, 3634.
7. (a) Mehta, G.; Padma, S. *Tetrahedron Lett.*, **1987**, 28, 1295. (b) Mehta, G.; Padma, S. *J. Am. Chem. Soc.*, **1987**, 109, 2212.
8. (a) Higuchi, H; Takatsu, K.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.*, **1982**, 23, 671. (b) Higuchi, H; Kobayashi, E.; Sakata, Y.; Misumi, S. *Tetrahedron* **1986**, 42, 1731.
9. Yang, N. C.; Horner, M. G. *Tetrahedron Lett.*, **1986**, 27, 543.
10. Gleiter, R.; Karcher, M. *Angew. Chem. Int. Ed. Engl.*, **1988**, 27, 840.
11. Cha, O. J.; Osawa, E.; Park, S. *J. Mol. Struc.*, **1993**, 300, 73.
12. Dailey, W. P. *Tetrahedron Lett.*, **1987**, 28, 5787.
13. Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.*, **1988**, 110, 2102.
14. Engelke R. *J. Am. Chem. Soc.*, **1986**, 108, 5799 and references therein.
15. Sakamoto, Y.; Miyoshi, N.; Shinmyozu, T. *J. Am. Chem. Soc.*, **1996**, 118, 12267 and references therein.
16. (a) Hübert, A. J. *J. Chem. Soc. C*, **1967**, 6. (b) Otsubo, T.; Kitasawa, M.; Misumi, M. *Bull. Chem. Soc. Jpn.*, **1979**, 52, 1515. (c) Meno, T.; Sako, K.; Suenaga, M.; Mouri, M.; Shinmyozu, T.; Inazu, T. *Can. J. Chem.*, **1990**, 68, 440.
17. Selected spectroscopic data and elemental analysis for **12**: mp 68.5-70.0 °C; ^{1}H NMR δ 1.23 (d, J = 11.9 Hz, 1H), 1.47 (d, J = 11.9 Hz, 1H), 1.41-1.73 (m, 11H), 1.64 (s, 1H), 1.82-2.09 (m, 7H), 2.07 (s, 2H), 2.14 (d, J = 6.3 Hz, 1H), 2.40 ppm (d, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, DEPT) δ 21.2 (sec.), 30.2 (sec.), 31.1 (sec.), 36.2 ((sec.), 37.4 (two sec.), 38.6 (sec.), 39.7 (tert.), 40.1 (sec.), 40.7 (sec.), 42.1 (sec.), 43.0 (quat.), 45.8 (quat.), 47.2 (tert.), 49.5 (tert.), 53.9 (tert.), 55.8 (quat.), 58.2 (quat.), 59.7 (quat.), 65.8 (tert.), 74.5 ppm (quat.). Anal. Calcd for $C_{21}H_{25}Cl$: C, 80.62; H, 8.05 %. Found: C, 80.42; H, 8.04 %.
18. Selected spectroscopic data and elemental analysis for **13**: mp 115.5-119.0 °C; ^{1}H NMR δ 1.34 (t, J = 1.6 Hz, 1H), 1.18-2.05 (m, 14H), 1.43 (d, J = 2.64 Hz, 2H), 2.15-2.48 (m, 4H), 2.33 (dd, J = 7.59 Hz, 1H), 2.53 (dd, J = 7.59 Hz, 1H), 2.79 (s, 1H), 5.12 (s, 1H), 5.60 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, DEPT)δ 20.3 (sec.), 26.3 (sec.) 28.2 (sec.), 33.8 (sec.), 33.9 (sec.), 34.4 (sec.), 35.4 (sec.), 35.7 (sec.), 39.1 (sec.), 42.8 (sec.), 51.8 (quat.), 52.2 (tert.), 54.8 (tert.), 61.5 (quat.), 64.5 (quat.), 67.0 (tert.), 75.5 (quat.), 136.0 (olefinic), 139.3 (olefinic), 141.3 (olefinic), 144.1 ppm (olefinic). Anal. Calcd for $C_{21}H_{26}O \cdot 1/4H_2O$: C, 84.37; H, 8.85 %. Found: C, 84.49; H, 8.85 %.
19. Selected spectroscopic data and elemental analysis for **14**: mp 69-71 °C; ^{1}H NMR δ 1.20 (d, J = 12.0 Hz, 1H), 1.28 (s, 1H), 1.35 (s, 1H), 1.41 (d, J = 12.0 Hz, 1H), 1.44-1.71 (m, 13H), 1.78-1.81 (m, 1H), 1.88-1.94 (m, 2H), 1.99-2.02 (m, 2H), 2.04 (d, J = 6.5 Hz, 1H), 2.06 (s, 2H), 2.14 ppm (d, J = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, DEPT) δ 19.5 (sec.), 29.4 (sec.), 30.4 (sec.), 35.4 (sec.), 36.4 (sec.), 36.8 (sec.), 37.8 (two sec.), 38.3 (tert.), 39.3 (sec.), 40.1 (sec.), 43.1 (quart.), 43.3 (quart.), 46.0 (tert.), 47.1 (tert.), 50.8 (tert.), 55.8 (quat.), 56.0 (quat.), 58.5 (quat.), 62.7 (tert.), 77.0 ppm (quat.). FABMS: m/z 294 (M^+). Anal. Calcd for $C_{21}H_{26}O \cdot 1/2H_2O$: C, 83.12; H, 8.97 %. Found: C, 83.16; H, 8.94 %.
20. The computations were performed with MM3-92, graphically facilitated by CAChe from Sony/Tektronics Co.. MM3-Program obtained from Technical Utilization Corporation. The program was developed by N. L. Allinger and coworkers, University of Georgia.