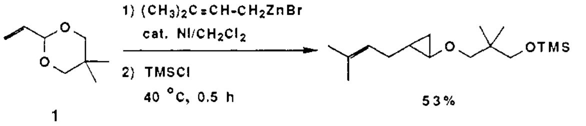
procedure of Normant[12] followed by allylation or allenylation proceeds smoothly (entries 4 and 5).

Upon heating, the zinc homoenolate was eliminated to give the α-alkylated α,β-unsaturated acetal. Such dehydrometalation could be suppressed completely below room temperature. Noteworthy is the fact that an additive TMSCl facilitates an intramolecular alkylation to afford exclusively the corresponding cyclopropanol derivative (eq 2).



1 (2)

Acknowledgment. Partial financial support from the Ministry of Education, Japanese Government, is gratefully acknowledged.

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(10) For alkylation of zinc homoenolate, see: (a) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. Oshino, H.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1985**, *50*, 2802. Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 83. Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056. (b) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 5559. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.* **1986**, *27*, 955. Ochiai, H.; Tamaru, Y.; Tsubaki, K.; Yoshida, Z. *J. Org. Chem.* **1987**, *52*, 4418. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157. Ochiai, H.; Nishihara, T.; Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1988**, *53*, 1343. Tamaru, Y.; Nakamura, T.; Sakaguchi, M.; Ochiai, H.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1988**, 610. For similar reactions, see: (c) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1988**, *29*, 2395. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.

(11) A representative experimental procedure is given by the prenylation–methylation sequence of 5,5-dimethyl-2-vinyl-1,3-dioxane (**1**) (entry 3 in Table II). To a solution of 3-methyl-2-butenylzinc bromide (0.88 mmol)[8] in CH_2Cl_2 (2 mL) was added catalytic $NiBr_2(PBu_3)_2$ (15.6 mg, 0.025 mmol) at 25 °C. After 10 min, 5,5-dimethyl-2-vinyl-1,3-dioxane (**1**) (35.6 mg, 0.25 mmol) was added at 25 °C, and the resulting mixture was stirred at 40 °C for 40 min. Zinc homoenolate, thus obtained, was methylated by adding a mixture of CH_3I (0.156 mL, 2.5 mmol) and HMPA (1.04 mL, 6 mmol) at 25 °C for 16 h. The mixture was poured into saturated NH_4Cl aqueous solution and extracted with ether. The combined extracts were dried and concentrated, and the product was purified by column chromatography on silica gel (AcOEt/hexane = 1:20) to give 5,5-dimethyl-2-(1′-ethyl-4′-methyl-3′-pentenyl)-1,3-dioxane (28.3 mg, 50% yield) as a colorless oil.

(12) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 4427, 4431, 5727.

Photochemical Generation of Bicyclo[4.2.2]decapentaene from [4.2.2]Propella-2,4,7,9-tetraene. Preference of [4]Paracyclopha-1,3-diene Structure over Bicyclo[4.2.2]deca-1,3,5,7,9-pentaene Structure

Takashi Tsuji* and Shinya Nishida

Department of Chemistry, Faculty of Science
Hokkaido University, Sapporo 060, Japan

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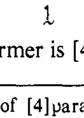
Geometrically distorted unsaturated compounds have attracted considerable attention in recent years. The hitherto unknown bicyclo[4.2.2]decapentaene is of particular interest because at least two unique alternative structures, namely, bicyclo[4.2.2]deca-1(8),2,4,6,9-pentaene (**1**) and -1,3,5,7,9-pentaene (**2**), are conceivable. The former is [4]paracyclophadiene,[1] whereas the latter may be viewed as 1,6-etheno bridged *cis,trans,cis,trans*-cyclooctatetraene.[2] Both structures feature two bridgehead double bonds and are expected to be highly reactive. In this communication we report that the photochemical transformation of [4.2.2]propella-2,4,7,9-tetraenes, **3a**[3] and **3b**,[4] leads to bicyclo[4.2.2]decapentaenes which are best represented by the structures **1a** and **1b**, respectively.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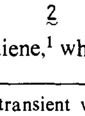
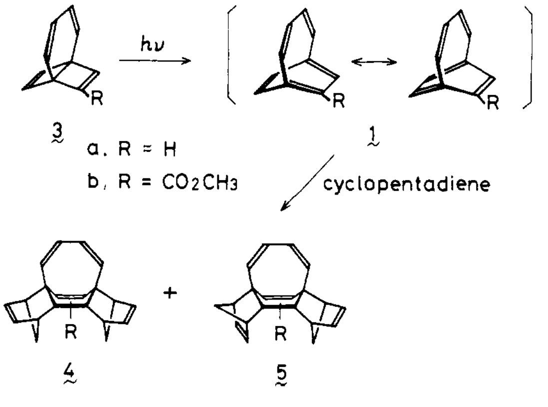

2

Irradiation of a mixture of **3a** and cyclopentadiene in hexane with a high pressure mercury lamp through Pyrex at 0 °C led to the formation of two 2:1 adducts of cyclopentadiene to **3a** (63% yield) in a ratio of ca. 1:2. The minor and major products were assigned as **4a** and **5a**, respectively, on the basis of their spectral data.[5] Thus, the cleavage of the central σ bond of **3a** and the subsequent Diels–Alder addition of two molecules of cyclopentadiene to the bridgehead double bonds of resultant **1a** were unambiguously established primarily by the following observations: (1) the ^1H NMR spectra of **4a** and **5a** each consisted of ten olefinic and ten aliphatic proton absorptions, (2) ^1H NMR signals characteristic of a norbornene ring, and (3) the very similar UV spectra of **4a** and **5a** showing λ_{max} at ca. 270 nm (ϵ ~4000) which indicated the intactness of the conjugated diene moiety of **3a**. The simple ^1H and ten line ^{13}C NMR spectra of the minor product were compatible only with a symmetrical structure, and close examination of the ^1H NMR permitted the assignment of **4a** as a diexo adduct. Virtually no volatile products other than **4a** and **5a** were detected in the product mixture. The photochemical reaction of **3b** with cyclopentadiene similarly afforded a mixture of **4b** and **5b** together with their secondary products[6] in a combined yield of 40%. In no case was any adduct derived from **2** detected.[7]



In addition to the aforementioned trapping experiments, the formation of **1** was supported by a spectroscopic study. When **3a** in an EPA[9] glass was irradiated with a low-pressure mercury lamp (254 nm) at 77 K, an absorption showing λ_{max} at 274 and 347 nm appeared (Figure 1a).[10,11] The species generated was stable at 77 K in the dark but underwent complete decomposition when the frozen glass was thawed below −100 °C. The transient was also photochemically susceptible, and, upon irradiation with

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[1] Generation of [4]paracyclophane as a transient was very recently confirmed. (a) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1189. *J. Am. Chem. Soc.* **1988**, *110*, 2157. (b) Kostermans, G. B. M.; Bobeldijk, M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471.

[2] *cis,trans,cis,trans*-Cyclooctatetraene is not yet known.

[3] Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1983**, *24*, 3361.

[4] Tsuji, T.; Komiya, Z.; Nishida, S. *Tetrahedron Lett.* **1980**, *21*, 3583.

[5] See Supplementary Material.

[6] Products via di-π-methane rearrangement and intramolecular [2 + 4] cycloaddition.[5]

[7] Examination of molecular models (FMM; Prentice-Hall: Englewood Cliffs, NJ) indicates that addition of two molecules of cyclopentadiene to the bridgehead double bonds of **2** is not sterically hindered and effectively relieves the steric strain inherent in **2**. It should also be pointed out that a bridgehead olefin of a related structure undergoes ready cycloaddition with cyclopentadiene.[8]

[8] Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194.

[9] A 5:5:2 mixture of ether, isopentane, and ethanol.

[10] The absorption spectra of the transients in Figure 1 were obtained by correcting difference spectra (before and after the 254-nm light irradiation) for the consumption of **3**. The conversion of **3a** determined by GLC using decane as an internal standard was 8% and that of **3b** using tetraglyme as an internal standard was 22%.

[11] Molar absorptivity at 274 nm was estimated to be ca. 5000.

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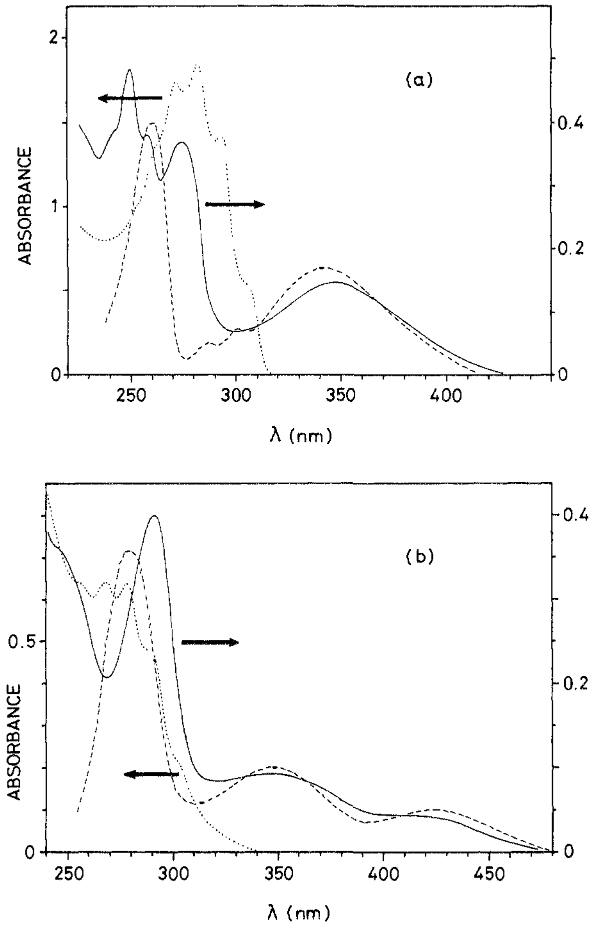
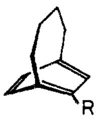


Figure 1. Electronic absorption spectra of **3** in EPA at 77 K prior to irradiation (dotted lines), transients generated upon irradiation of **3** with 254-nm light (solid lines),[10] and **6**[1a,13] (dashed lines): (a) R = H; (b) R = CO_2CH_3. Small peaks at 285 and 300 nm in the spectrum of **6a** are due to *p*-xylylene.[1a]

366-nm light, the developed absorption was efficiently bleached and the absorption spectrum of **3a** was largely restored. This behavior was reminiscent of [4]paracyclophane (**6**)[1a] and suggested



6

that the intermediate photochemically reverted to **3a**. Irradiation of **3b** in an EPA glass with 254-nm light at 77 K also led to a species which showed λ_{max} at 291, 345, and 415 (sh) nm in the UV-vis spectrum (Figure 1b)[10,12] and thermal and photochemical behavior similar to that observed above. In Figure 1 are also shown the absorption spectra of **6a** and **6b** which we recently reported.[1a] The striking similarity in shape of the presently observed spectra to those of the corresponding **6** in the long wavelength region (>265 nm)[13] indicates that the transient species produced here would certainly be **1**. In **1**, the π bond system in the four carbon bridge and that of the extremely bent benzene ring are nearly orthogonal to each other, and there could be little interaction between them.[14] If the species generated had the structure of **2**, the observed spectra would be much different from those of **6a** and **6b**. In **2**, the π bonds overlap each other only weakly, and such a poorly conjugated system tends to exhibit a broad, weak absorption spectrum.[15] Cyclooctatetraene is a notable example,[16] and the π bond system of **2** may be viewed as that of cyclooctatetraene perturbed by the etheno bridge double bond.

Thus, on the basis of the regioselective addition of cyclopentadiene to give **4** and **5** and the transient absorption spectra remarkably similar in shape to those of the corresponding **6**, it may be concluded that the irradiation of **3** leads to a species which is best represented by the structure **1**. This conclusion, however, does not rule out the possibility that the structure **2** represents a local minimum on the potential energy surface of bicyclo[4.2.2]decapentaene and may even be more stable than **1**, though the present photoreaction of **3** provided no evidence suggesting that such was the case. If **1** were less stable than **2**, **1** would be separated from **2** by a sizable energy barrier (>6 kcal/mol) since the absorption spectra of **1a** and **1b** showed no sign of decay within 1 h at 77 K.

Because a 1,3-butadienylene bridge is shorter and less flexible than a tetramethylene chain, the benzene ring in **1** will be more severely bent than that in **6**. Thus **1** will represent the most strained of the [*n*]paracyclophanes known so far.[1]

Supplementary Material Available: Spectroscopic data for **4a**, **4b**, **5a**, **5b**, and the secondary products (6 pages). Ordering information is given on any current masthead page.

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(12) Molar absorptivity at 291 nm was estimated to be ca. 9000.

(13) In the short wavelength region (<265 nm), **1** exhibited peaks which would be due to the diene chromophore in the bridge. Since molar absorptivity of 6 has not yet been determined, the absorption intensity of the spectrum of 6 was adjusted to that of 1 in Figure 1.

(14) When the π electron systems of formally conjugated chromophores are at right angles to each other and do not interact, the observed spectrum will appear to be a summation of the spectra of the separate chromophores.[15]

(15) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 15.

(16) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1. (b) Cope, A.; Bailey, W. J. *J. Am. Chem. Soc.* **1948**, *70*, 2305.

New Types of Metallacycles Formed by Cycloaddition of Imines and $\mathrm{Bu^tN{=}O}$ with Mn and Re Carbyne Complexes

Beth M. Handwerker, Kevin E. Garrett, and
Gregory L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, University of Delaware
Newark, Delaware 19716

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Carbene complexes have found an impressive synthetic utility in organic chemistry through a variety of carbene transfer and cycloaddition reactions.[1] In contrast, carbyne complexes have far fewer applications, partly because their overall chemistry is significantly less developed.[2] For example, the only well-demonstrated cycloaddition reaction is with alkynes to form metallacyclobutadienes,[1,3] although transient metallacycles may form in reactions of metal carbynes with isocyanates,[4] nitriles,[5] ketones,[5] and aldehydes.[5] We have examined the cycloaddition behavior

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 16.

(2) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51.

(3) (a) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046. (b) Pederson, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808. (c) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

(4) Gill, D. S.; Baker, P. K.; Green, M.; Paddick, K. E.; Murray, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 986.

(5) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398.

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