5284 *J. Am. Chem. Soc.* **1993,** *115,* 5284–5285

Communications to the Editor

[1.1]Paracyclophane. Spectroscopic Evidence for Generation of the Bis(methoxycarbonyl) Derivative

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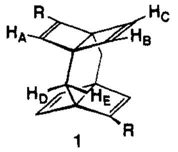
Received March 11, 1993

[2.2]Paracyclophane was first isolated in 1949,[1] and its structure, in which benzene rings are bent and aligned in parallel in close proximity, fascinated chemists. Despite the extensive exploration of the chemistry of cyclophanes[2] and considerable interest in strained comopounds,[3] the lower [1.2] and [1.1] homologues have remained unknown. We report here the photochemical generation of the first [1.1]paracyclophane derivative **2b** from **1b** and the results of ^{1}H NMR and UV/vis spectroscopic studies.



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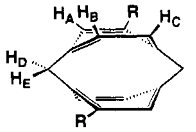

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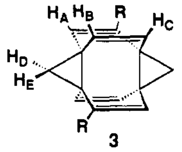

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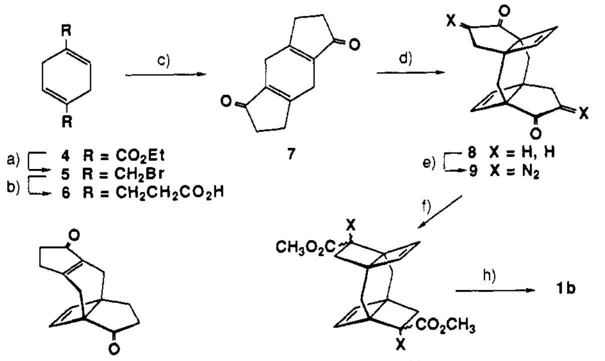
a, R = H; **b**, R = CO_2CH_3

Synthesis of bis(Dewar benzene) compound **1b** was achieved as outlined in Scheme I. The $(CF_3CO)_2O$-induced double cyclization of **6**, which was prepared from **4**[4] in five steps, cleanly afforded **7**. The photocycloaddition of acetylene to **7** stereoselectively occurred to produce **8** as the single diacetylene [2 + 2] adduct. The anti stereochemistry assigned to **8** on the basis of NOE experiments was later confirmed by the same experiments on **1b**.[5] The subsequent conversion of **8** into **1b** was accomplished according to the procedure previously reported for the preparation of Dewar benzene derivatives.[6] Compound **1b** was obtained in about 1% yield overall in 11 steps from **4**.

Irradiation of **1b** in EPA glass[7] with a 254-nm light source at 77 K led to the development of absorption showing λ_{max} at 256, 348, and 405 nm and extending to 480 nm (Figure 1, spectrum A). The generated species was photochemically labile and efficiently consumed when irradiated with >390-nm light, which was not absorbed by **1b** (spectrum B). The difference spectrum between spectra A and B indicated that the initial product was converted to the species exhibiting λ_{max} at 267 nm (spectrum C).

Scheme I[a]



[a] (a) LAH and then PBr_3; (b) AcO*t*-Bu/LDA and then CF_3CO_2H; (c) $(CF_3CO)_2O/BF_3{\cdot}OEt_2/CH_2Cl_2$; (d) *hν*, C_2H_2/acetone–CH_2Cl_2; (e) $HCO_2Et/NaOEt$ and then TsN_3/Et_3N; (f) *hν* in MeOH; (g) LDA and then PhSeBr; (h) H_2O_2.

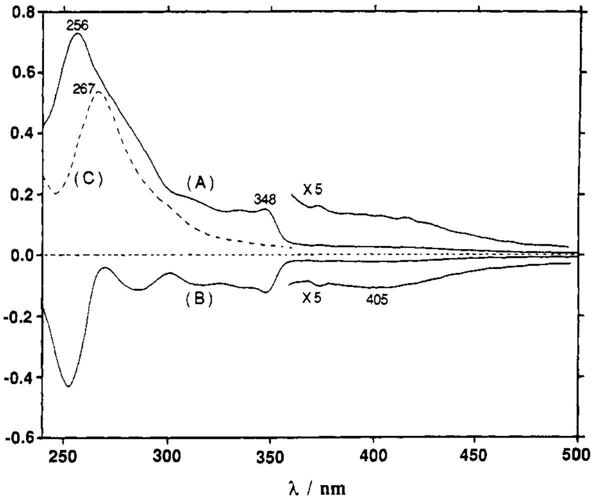


Figure 1. Difference UV/vis spectra (A) between the absorptions before and after the irradiation of **1b** and (B) between those before and after further irradiation with >390-nm light (see text for conditions). Spectrum C was obtained by adding spectrum B to spectrum A.

Table I. ^{1}H NMR Parameters for **1b**, **2b**, and **3b**[a]

species	$H_A(\delta)$	J_{AB}(Hz)	$H_B/H_C(\delta)$	J_{BC}(Hz)	$H_D/H_E(\delta)$	J_{DE}(Hz)
1b	7.19	<1	6.45, 6.56	2.4	2.38, 2.50	14.6
2b	7.60	2.5	6.95, 7.14	8.8	4.44[b]	11.7
3b	7.12	<1	6.03, 6.13	6.4	1.95, 2.45	6.6

[a] In THF-d_8 at –60 °C. The signals of OCH_3 were observed at δ 3.65, 3.94, and 3.61 for **1b**, **2b**, and **3b**, respectively. [b] The signal of the other proton could not be identified.

The ^{1}H NMR spectrum of C_i symmetric **1b**[8] is simple and consists of two singlets (H_A and OCH_3) and two pairs of AX doublets (H_B/H_C and H_D/H_E). Irradiation of **1b** in THF-d_8 with 254-nm light at –70 °C gave rise to the observation of two sets of new signals, as listed in Table I. Their simple spectra, chemically shifted from but closely similar to that of **1b**, indicated that the C_i symmetry was retained in both of the generated species. Increases in the vicinal coupling between the olefinic protons H_B

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(1) (a) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *164*, 915–916. (b) Brown, C. J. *J. Chem. Soc.* **1953**, 3265–3270.

(2) (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204–213. (b) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983. (c) *Cyclophanes I* and *II* (*Topics in Current Chemistry 113* and *115*); Vögtle, F., Ed.; Springer-Verlag: Berlin, 1983. (d) Vögtle, F. *Cyclophan-Chemie*; B. G. Teubner Verlag: Stuttgart, 1990.

(3) (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322. (c) Synthesis of Non-natural Products: Challenge and Reward (Tetrahedron Symposia-in-print 26); Eaton, P. E., Ed.; *Tetrahedron* **1986**, *42*, 1549–1915. (d) The July/August 1989 issue of *Chemical Reviews* reports exclusively on strained organic compounds.

(4) Jones, D. G. Ger. Patent 950 285, 1956; *Chem. Abstr.* **1959**, *53*, 17926.

(5) According to force field calculations, the central six-membered ring in the mono adduct **12** is preferentially bent toward the cyclobutene ring as depicted. Prevailing steric factors would thus guide the entry of the second acetylene anti to the first one. The calculations were performed with *Chem3D Plus*, Ver. 3.0; Cambridge Scientific Computing: Cambridge, MA, 1990.

(6) Tsuji, T.; Komiya, Z.; Nishida, S. *Tetrahedron Lett.* **1980**, *21*, 3583–3586.

(7) A 5:5:2 mixture of ether, isopentane, and ethanol.

(8) At least on the ^{1}H NMR time scale.

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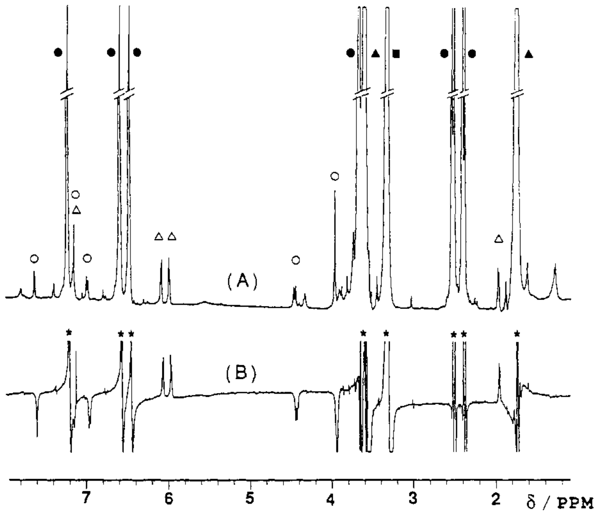
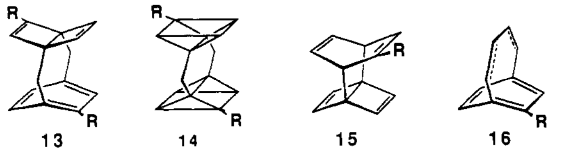


Figure 2. (A) 500 MHz ^1H NMR spectrum observed upon irradiation of **1b** in THF-d_8 with 254-nm light at -70 °C: (●) **1b**; (▲) THF-d_n; (■) H_2O; (○) **2b**; (△) **3b**. (B) Difference spectrum obtained by further irradiating the mixture with >390-nm light. Peaks marked with an asterisk are the residual signals of **1b**, H_2O, and the solvent due to subtraction error.

and H_C from small 2.4 Hz, characteristic of cyclobutene,[9a] to 8.8 Hz in one and 6.4 Hz in the other suggested the cleavage of the central bonds of both of the Dewar benzene moieties in both the products. None of the less symmetrical products resulting from the rearrangement of only one of the Dewar benzenes, e.g., **13**, was formed in a detectable amount. Upon irradiation of the resultant NMR sample with >390-nm light, one set of signals was enhanced at the sacrifice of the other, as clearly exhibited in the difference spectrum (Figure 2). This implied that the latter was due to the species responsible for the UV/vis absorption extending to 480 nm and the former to the one showing λ_{max} at 267 nm.

These observations seem to be best and only accommodated by assuming the initial rearrangement of **1b** into **2b**, which was in turn transformed into **3b** via the transannular photocycloaddition.[10] Bis(prismane) derivative **14**, another plausible C_i symmetric product, is apparently incompatible with either set of the ^1H NMR signals.[11] The assignment of the long-wave electronic absorption to **2b**, which possesses strongly interacting bent benzene chromophores, seems reasonable. The observation of substantial coupling between H_A and H_B of **2b** is also consistent with the aromatization of the Dewar benzenes. Interestingly, the aromatic ring protons H_{A-C} of **2b** resonate ~0.45–0.50 ppm downfield from the corresponding protons of [2.2]paracyclophane derivative.[12] The upfield shifts of the methylene proton signals from δ ~4 to 1.95 and 2.45 and the decrease in their mutual coupling from normal (11.7 Hz) to the value (6.6 Hz) typical of cyclopropyl derivatives[9] upon the secondary photolysis are consistent with the proposed transformation. The UV absorption band at 267 nm is also compatible with **3b**.[13] To our knowledge, the production of **3b** from **2b** represents the first direct formation of benzene *p,p*-dimer. One may argue that the UV/vis absorption extending to 480 nm might be due to **13**, a [4]paracyclophane derivative. Such a possibility, however, may be ruled out because the observed spectrum is markedly different from that which we previously reported for **16**.[14]



13 14 15 16

$R = CO_2CH_3$

The UV/vis absorption of **2b** remained unchanged for 3 h at -20 °C but had largely decayed after 1 h at room temperature, suggesting that the stability of **2b** at ambient temperature is only marginal. Compound **3b** is also thermally and photochemically labile. Thus, **3b** was rapidly consumed when irradiated with 254-nm light or when its solution in THF-d_8 was allowed to stand at room temperature in the dark.

Supplementary Material Available: Yields and spectroscopic data for **1b** and **4–11** (5 pages). Ordering information is given on any current masthead page.

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[9] (a) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed.*; Pergamon Press: Oxford, England, 1969. (b) Morris, D. G. In *The Chemistry of Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley & Sons: Chichester, England, 1987; pp 101–172.

[10] The concentration of **2b** remained relatively low, owing to its photoreactivity coupled with the high molar absorptivity at 254 nm.

[11] The ^1H NMR spectrum A in Figure 2 was recorded after ca. 10% of **2b** was consumed. The yields of **2b** and **3b** were estimated to be about 30% and 60%, respectively, on the basis of their signal intensities. The formation of **14** would be relatively minor at best.

[12] For the H_{A-C} of the [2.2]paracyclophane homologue, values of δ 7.17 (d, J = 1.8 Hz), 6.68 (dd, J = 7.7, 1.8 Hz), and 6.51 (d, J = 7.7 Hz) have been reported. Hopf, H.; Lenich, F. T. *Chem. Ber.* **1974**, *107*, 1891–1902.

[13] Compound **15** exhibits λ_{max} at 274 nm. Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1983**, *24*, 3361–3364.

[14] (a) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1988**, *110*, 2157–2164. (b) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368–369.