Communications

Oxidative Photocyclization of Tethered Bifluorenylidenes and Related Compounds†

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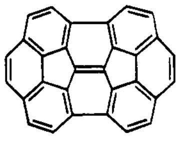
Recent advances in fullerene chemistry have provoked an ever burgeoning interest in bowl-like polycyclic aromatic hydrocarbons.[1-4] The key step used in the synthesis of these compounds involves either a pyrolytic or a photocatalyzed pericyclic process. Various circulenes are prepared by these methods.[1] More recently, the synthesis of **1** has been achieved by flash vacuum pyrolysis.[3d] Alternatively, the dehydrogenative cyclization of a bifluorenylidene-related compound **2** or **3** may also furnish an intriguing approach for the synthesis of **1** or **4**, respectively. Indeed, thermal dehydrocyclization of **3** above 700 °C yields **6** which can further cyclize to **4** at elevated temperature.[4] In addition, pyrolysis of **2** gives **5** as one of the products.[4] However, the yields in general are low. Since oxidative photocyclization of stilbene derivatives giving the corresponding phenanthrene skeleton has been extremely useful for the synthesis of polycyclic aromatic compounds,[1,5] the use of such tactics appears conceivable for the cyclization of **2** or **3**. The photochemistry of bifluorenylidene **3** has been investigated briefly; none of the cyclization product **6** has been detected, however.[6,7] In this paper, we disclose an unprecedented successful approach for the synthesis of derivatives of **5** and **6** by photochemical procedures.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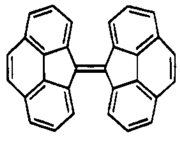
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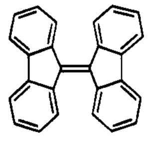
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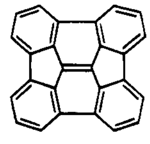
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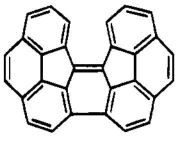
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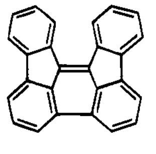
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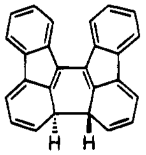

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Bifluorenylidene **3** is nonplanar, and the dihedral angle between the two fluorene moieties is 32.9°.[8] The distance between C_1 and $C_{1'}$ is approximately 320 pm, which is in the "correct" range for the photocyclization of two π-systems.[9] Since the pericyclic reaction is reversible, the initial cyclized product **7** is apparently much more strained than the starting **3**. Indeed, MNDO calculations suggested that **7** is more strained by 18 kcal/mol than **3**. Accordingly, it is not surprising that the conversion of **3** into **6** or related reactions has not been successful.[6,7]

We recently reported a convenient synthesis of a 2,2′-tethered bifluorenylidene **9** by intramolecular desulfurdimerization of the corresponding bisdithioacetals **8** (eq 1).[10,11] The X-ray analysis of **9a** ($n = 1$) indicates a distance of 270 pm between C_1 and $C_{1'}$. Furthermore,

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† Dedicated to the memory of the late Professor Hidemasa Takaya of Kyoto University.

(1) For a review on circulenes, see: Yamamoto, K.; Matsubara, H. *J. Synth. Org. Chem.* **1995**, *53*, 318.

(2) [5]-Circulene: (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730. (c) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (d) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920. (e) Borchardt, A.; Fuchicello, A.; Kilwary, K. V.; Balbridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921. [7]-Circulene: (f) Jessup, P. J.; Reiss, J. A. *Aust. J. Chem.* **1977**, *30*, 851. (g) Jessup, P. J.; Reiss, J. A. *Aust. J. Chem.* **1976**, *29*, 173. (h) Jessup, P. J.; Reiss, J. A. *Tetrahedron Lett.* **1975**, 1453. (i) Yamamoto, K.; Harada, T.; Nakazaki, M.; Nakao, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171. (j) Yamamoto, K.; Harada, H.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578.

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(4) (a) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Tetrahedron Lett.* **1994**, *35*, 7013. (b) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycycl. Arom. Compds* **1995**, *4*, 209.

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(7) The photocyclization of **3** giving **6** has been claimed but not well characterized. However, the ^{1}H NMR data [δ 7.47–7.87 (1 H) and 6.87–7.42 (3 H)] of their compound do not appear to be consistent with the skeleton **6** (cf. De Gunst, G. P. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 801). As can be seen in ref 12, our ^{1}H NMR data indicated that these compounds should exhibit a low field signal at δ 8.5–8.6 for the absorptions of H_1's for **11a** and **b** and also for **20a** (cf. ref 4).

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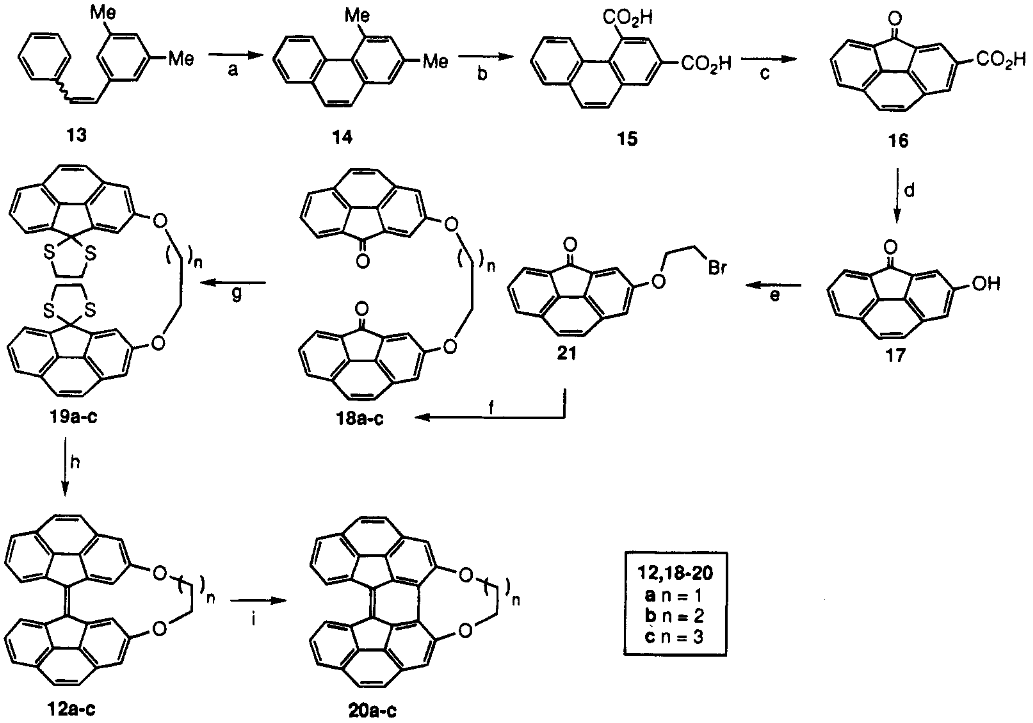
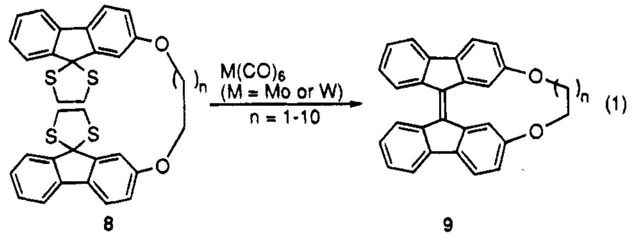
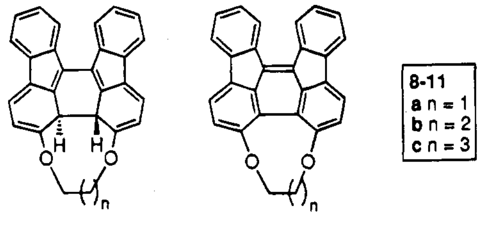
Scheme I[a]



[a] Key: (a) $h\nu$, I_2, benzene, 12 h; 84%; (b) (i) NBS(2.3 equiv), benzene, reflux 14 h; (ii)DMSO, $NaHCO_3$, 160 °C; (iii) $AgNO_3$, KOH, rt, 24 h; 50%; (c) (i) $SOCl_2$, py, 12 h; (ii) $AlCl_3$, $PhNO_2$, rt; 85%; (d) (i) $SOCl_2$; (ii) NaN_3, n-Bu_4NBr; (iii) benzene, reflux 6 h; (iv) H^+/H_2O; (v) HCl(concd), $NaNO_2$, H_2SO_4(concd); 35%; (e) $BrCH_2(CH_2)_nBr$, K_2CO_3, DMF; **18a**: 46%; **18b**: 84%; **18c**: 61%; (f) **17**, K_2CO_3, DMF; combined yield of **18a**; 79%; (g) BF_3OEt_2, $HSCH_2CH_2SH$; **19a**: 90%; **19b**: 90%; **19c**: 87%; (h) $Mo(CO)_6$ or $W(CO)_6$, PhCl; **12a**: 24%; **12b**: 38%; **12c**: 64%; (i) $h\nu$, PhSeSePh, PhH; **20a**: 50%.





MNDO calculations interestingly showed that **10a** was only 5.5 kcal/mol more strained than its precursor **9a**. Consequently, **9a** might demonstrate a useful entry to test the applicability for this photocyclization reaction. Hence, **9a** in benzene in the presence of excess I_2 was subject to irradiation using a Hanovia 450W photochemical reactor for 8 h. After usual workup and chromatographic separation, **11a** was obtained in 50% yield.[12] The less strained **9b** gave **11b** in only 6% yield under the same conditions.[13] As expected, starting material was recovered from the reaction of **9c** under similar conditions.[13]

Having been successful in the photocyclization of bifluorenylidene derivatives, our next goal was to synthesize the bisbenzoannulated analogues **12a–c** which were prepared from **13** (Scheme 1). It is noteworthy that **12a** was highly reactive and decomposed at room temperature in $CDCl_3$ solution. Accordingly, as soon as the desulfurdimerization reaction was carried out, after flashing through a short silica gel column, the mixture was subject to the photolysis in the presence of PhSeSePh for 30 min. The resulting mixture was purified by chromatography, giving the desired photocyclized product **20a** in 12% overall yield.[12] No cyclization, however, was observed for **12b** and **c** under similar conditions, and the starting material was recovered.

In summary, we have demonstrated the first example using oxidative photochemical reactions to cyclize the 2,2′-tethered bifluorenylidene derivatives. This procedure has paved a new path for the synthesis of bowl-shaped polycyclic aromatic hydrocarbons. Further extension is in progress in our laboratory.

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Supporting Information Available: Experimental procedures and spectral data for **11a**, **b**, **12b**,**c**, and **20a** (8 pages).

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[12] ^1H NMR data: **11a**: δ (400 MHz, $CDCl_3$) 4.49 (s, 4 H), 7.41 (d, J = 7.8 Hz, 2 H), 7.44–7.48 (m, 4 H), 7.87–7.92 (m, 4 H, containing a doublet at δ 7.91, J = 7.8 Hz), 8.50–8.54 (m, 2 H). **11b**: δ (200 MHz, $CDCl_3$) 1.99 (m, 2 H), 4.60–4.63 (m, 4 H), 7.46–7.50 (m, 4 H), 7.51 (d, J = 7.7 Hz, 2 H), 7.91–7.93 (m, 4 H), 8.00 (d, J = 7.7 Hz, 2 H), 8.58–8.62 (m, 2 H). **20a**: δ (300 MHz, $CDCl_3$) 4.67 (4H, s), 7.78 (dd, J = 7.5 Hz, 7.9 Hz, 2 H), 7.80 (s, 2 H), 7.88 (d, J = 8.8 Hz, 2 H), 7.95 (d, J = 8.8 Hz, 2 H), 7.98 (d, J = 7.9 Hz, 2 H), 8.51 (d, J = 7.5 Hz, 2 H).

[13] The MNDO calculated strain energy difference between **9b** and **10b** was 10 kcal/mol and that between **9c** and **10c** 17 kcal/mol.