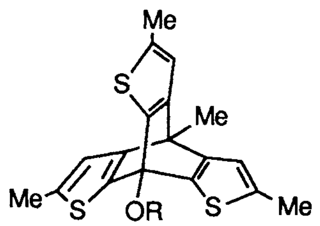
CHEMISTRY LETTERS, pp. 681-684, 1993.
© 1993 The Chemical Society of Japan

Photorearrangement of Thiophenetriptycene1)

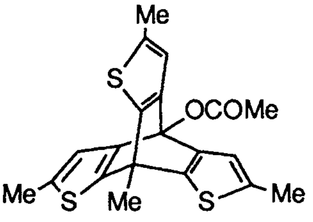
Akihiko ISHII, Kiyoto MAEDA, Juzo NAKAYAMA,* and Masamatsu HOSHINO
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338

Photoirradiation of 4,8-dihydro-4,8[3',2']thiophenobenzo[1,2-*b*:5,4-*b'*]dithiophenes (thiophenetriptycenes) results in di-π-methane rearrangement to provide the corresponding semibullvalenes. In the initial stage of the di-π-methane rearrangement, C(7a)-C(8a) bridging occurs exclusively regardless of bridgehead substituents.

The photochemistry of barrelene and its benzo derivatives has been attracting much attention for recent 30 years. It is well documented that barrelene and benzo- and dibenzobarrelenes isomerize to the corresponding semibullvalenes by di-π-methane rearrangement.2) Recently we reported the first synthesis of the thiophene analogue of triptycene (thiophenetriptycene) **1a**.3) It is of interest to investigate the photolysis of thiophenetriptycenes for comparison with that of triptycenes4) and other heteroaromatic-fused barrelenes.5) Here we report the photorearrangement of **1a**, its derivatives **1b-c**, and the isomer **2**.6)



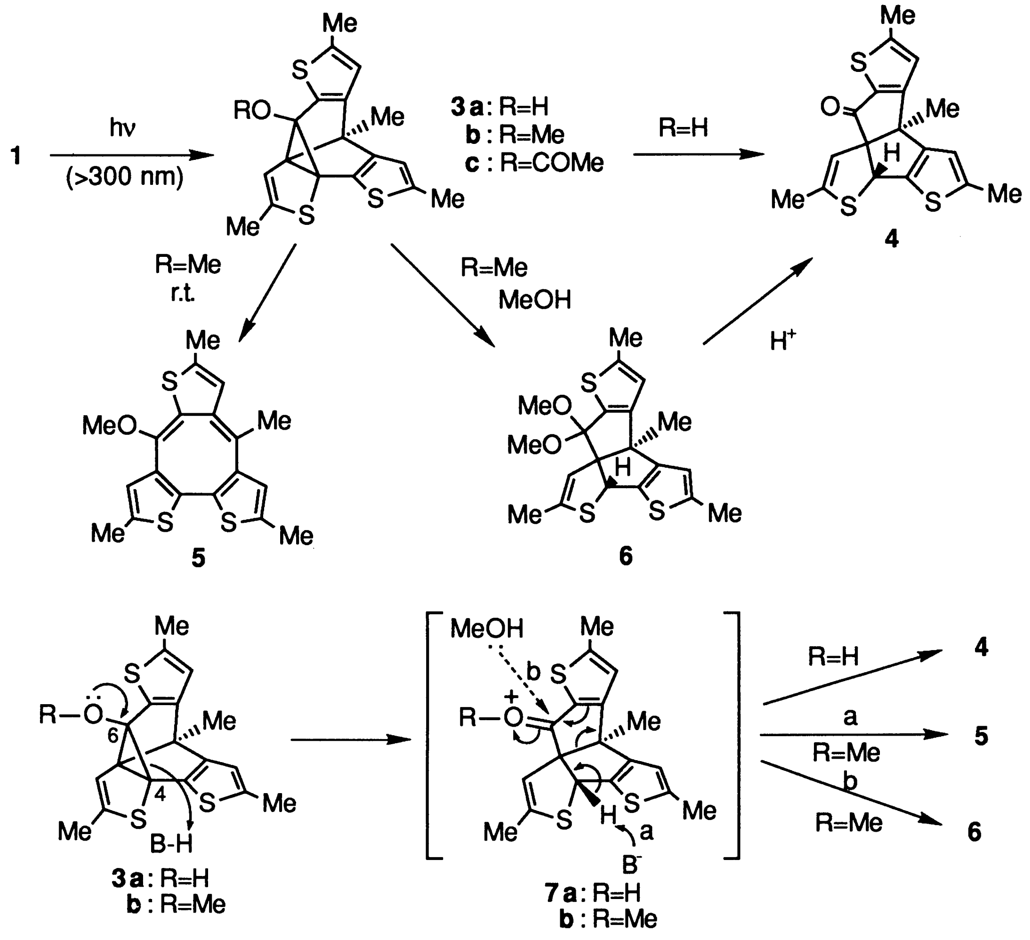
1 a : R=H
b : R=Me
c : R=COMe



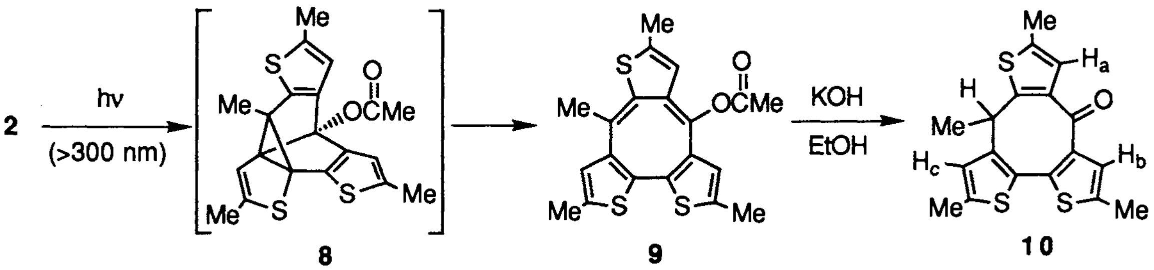
2

A solution (0.018 mol dm^{-1}) of **1a** (λ_{max} 303 nm, log ε 3.70) in benzene was irradiated at 5 °C by a high-pressure mercury lamp through a Pyrex filter. Evaporation of the solvent followed by purification by column chromatography (silica gel) gave a sole product (90%), the structure of which was assigned to **4** by the spectroscopic data7) and the X-ray crystal structure analysis.6) The ketone **4** is considered to be produced by a ring opening of the cyclopropanol ring of di-π-methane rearrangement product **3a**.8) Although the generation of carbenes has been proved in the photolysis of triptycenes,4) irradiation of **1a** in methanol gave only **4** (58%), indicating no generation of the corresponding hydroxycarbene.9,10)

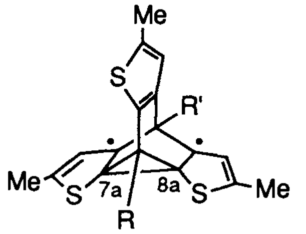
Photolyses of **1b-c** were next examined with expectation of direct observation of di-π-methane rearrangement products. A solution of **1b** in C_6D_6 was irradiated at 5 °C in an NMR tube for 15 min and then analyzed by ^{1}H NMR. The spectrum showed a new set of signals assignable to **3b** together with unchanged **1b** (the ratio of **3b**:**1b** was 1:1.2). The compound **3b** was unstable at room temperature and gradually isomerized to a cyclooctatetraene **5**. In a preparative scale, irradiation of **1b** at 0 °C for 1.5 h and then standing of the resulting solution in the dark at room temperature for 12 h yielded **5** in 48% isolated yield. On the other hand, addition of excess methanol to a solution of **3b** at 0 °C provided an acetal **6** in 58% yield. The acetal **6** was readily hydrolyzed to **4** by treatment with acid. The isomerizations of **3a** to **4** and **3b** to **5** and the reaction of **3b** with methanol might be caused by cleavage of the C(4)-C(6) bond catalyzed by acidic contaminants,[11] although bicyclo[3.3.0]octadienyls were proposed as intermediates in the isomerization of semibullvalenes to the corresponding cyclooctatetraene under photolytic or FVP conditions.[12] The resulting intermediate **7a** would give rise to **4**, while **7b** would afford either **5** with formation of a bithienyl linkage (path a) or **6** by attack of methanol on the carbocationic center (path b). An alternative attempt was made to obtain a di-π-methane rearrangement product by irradiation of **1c**. It is known that π-electron accepting substituents stabilize cyclopropane rings, while π-electron donating ones destabilize them;[13] an acetoxy group is a weaker π-electron donor than hydroxy and methoxy groups. As expected, irradiation of **1c** in benzene gave **3c** in 90% yield. All spectroscopic data support the structure. The semibullvalene **3c** purified by column chromatography (Al_2O_3) gradually decomposed to **4** in a solution and even if stored in a refrigerator in solid form.



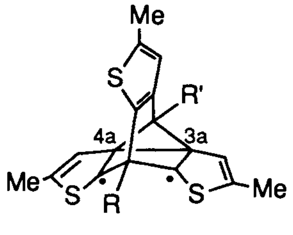
In order to know the effect of bridgehead substituents, photolysis of **2** was examined. Irradiation of **2** in benzene (0.0045 mol dm^{-1}) for 2 h gave **9** in 52% yield. The structure of **9** was identified by the spectroscopic data and a chemical transformation. Thus, hydrolysis of **9** in KOH-MeOH-CH_2Cl_2 gave **10** in 63% yield. In the ^1H NMR of **10**, two aromatic protons, H_a and H_b, were deshielded by the carbonyl (δ 7.16 and 7.47) and also 24% NOE enhancement of the signal intensity of another aromatic proton H_c (δ 6.74) was observed on irradiation of the aliphatic methyl. In contrast to photolyses of **1**, that of **2** was slower probably due to steric hindrance of the bridgehead methyl at the initial bridging.[4c)] Compound **9** might be formed by a ring opening of **8**, where a mechanism analogous to that of **3b** should be operative.



The results described above reveal undoubtedly that the C(7a)-C(8a) bridging occurs in the initial stage of the di-π-methane rearrangment of thiophenetriptycenes regardless of the bridgehead substituents, indicating the biradical intermediate **11** are more favorable than **12** produced by the C(3a)-C(4a) bridging because the formers are stabilized by conjugation with the double bonds.[14)]



11



12

References

1) We call 4,8-dihydro-4,8[3',2']thiophenobenzo[1,2-*b*:5,4-*b'*]dithiophene "thiophenetriptycene" for convenience.

2) H. E. Zimmerman, "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press (1980),Vol. 3, pp. 131-166.

3) A. Ishii, M. Kodachi, J. Nakayama, and M. Hoshino, *J. Chem. Soc., Chem. Commun.*, **1991**, 751.

4) a) H. Iwamura and K. Yoshimura, *J. Am. Chem. Soc.*, **96**, 2652 (1974); b) H. Iwamura and H. Tukada, *Tetrahedron Lett.*, **1978**, 3451; c) M. Iwamura, H. Tukada, and H. Iwamura, *ibid.*, **21**, 4865 (1980); d) M. Iwamura, E. Mori, A. Koike, T. Kitagawa, N. Koga, and H. Iwamura, *Chem. Lett.*, **1992**, 2051.

5) C.-C. Liao and P.-H. Yang, *Tetrahedron Lett.*, **33**, 5521 (1992) and references cited therein.

6) Unpublished results. Preparation of **1b**, **1c**, and **2** will be reported in the near future.

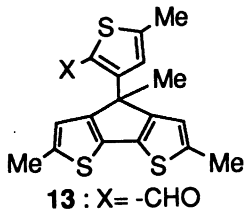
7) All new compounds (except for **3b**) gave satisfactory analytical and spectral data (q' means an incomplete quartet and quaternary carbon is abbreviated to C). **3b**: ^{1}H NMR δ (C_6D_6) 1.56 (s, 3H), 1.75 (d, *J*=1.3 Hz, 3H), 1.87 (d, *J*=0.9 Hz, 3H), 1.95 (d, *J*=0.9Hz, 3H), 3.56 (s, 3H), 5.23 (q, *J*=1.5 Hz, 1H), 6.08 (q, *J*=1.0 Hz, 1H), 6.19 (d, *J*=1.0 Hz, 1H). **3c**: ^{1}H NMR δ ($CDCl_3$) 1.70 (s, 3H), 2.00 (d, *J*=1.3 Hz, 3H), 2.18 (s, 3H), 2.29 (d, *J*=0.7 Hz, 3H), 2.32 (d, *J*=0.7 Hz, 3H), 5.41 (q', *J*=1.4 Hz, 1H), 6.28 (q', *J*=0.9 Hz, 1H), 6.35 (q', *J*=0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.8 (CH_3), 16.2 (CH_3), 16.3 (CH_3), 16.4 (CH_3), 20.6 (CH_3), 56.2 (C), 62.2 (C), 72.3 (C), 91.1 (C), 111.4 (CH), 116.4 (CH), 116.7 (CH), 128.8 (C), 131.9 (C), 144.1 (C), 144.4 (C), 144.8 (C), 155.6 (C), 158.5 (C), 170.3 (C). **4**: ^{1}H NMR δ

($CDCl_3$) 1.53 (s, 3H), 2.06 (d, *J*=1.1 Hz, 3H), 2.43 (br s, 3H), 2.56 (d, *J*=0.8 Hz, 3H), 5.10 (q', *J*=1.2 Hz, 1H, vinyl), 5.51 (s, 1H, methine), 6.56 (br s, 1H), 6.63 (q', *J*=0.9 Hz, 1H); ^{13}C NMR δ ($CDCl_3$) 16.3 (q), 16.8 (q), 17.2 (q), 23.2 (q), 56.0 (s), 57.1 (d), 91.6 (s), 115.6 (d), 118.3 (d), 120.6 (d), 134.4 (s), 139.0 (s), 143.3 (s), 146.5 (s), 148.1 (s), 159.7 (s), 174.5 (s), 195.3 (s). **5**: ^{1}H NMR δ ($CDCl_3$) 1.99 (s, 3H), 2.06 (s, 3H), 2.44 (s, 6H, 2xMe), 3.50 (s, 3H), 6.05 (q', *J*=1.5 Hz, 1H), 6.38 (q', *J*=1.0 Hz, 1H), 6.43 (q', *J*=1.0 Hz, 1H); δ (C_6D_6) 1.78 (s, 3H), 1.83 (s, 3H), 1.92 (d, *J*=0.8 Hz, 3H), 2.05 (d, *J*=0.8 Hz), 3.20 (s, 3H), 5.97 (d, *J*=1.4 Hz, 1H), 6.13 (s, 1H), 6.25 (d, *J*=1.0 Hz, 1H); ^{13}C NMR δ ($CDCl_3$) 15.5 (CH_3), 17.2 (CH_3), 22.4 (CH_3), 58.4 (CH_3), 120.9 (CH), 125.4 (CH), 126.4 (C), 127.4 (CH), 127.8 (C), 129.3 (C), 134.1 (C), 136.4 (C), 139.5 (C), 141.8 (C), 141.9 (C), 142.3 (C), 146.0 (C), 147.2 (C); UV (MeCN) λ_{max}/nm 407 (log ε 3.06), 305 (4.01), 269 (4.38), 231 (4.26). **6**: ^{1}H NMR δ ($CDCl_3$) 1.49 (s, 3H), 1.97 (d, *J*=0.9 Hz, 3H), 2.39 (d, *J*=0.8 Hz, 3H), 2.42 (s, 3H), 3.31 (s, H), 3.48 (s, 3H), 5.20 (s, 1H), 5.52 (d, *J*=1.4 Hz, 1H), 6.40 (d, *J*=0.9 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR δ ($CDCl_3$) 16.1 (CH_3), 16.3 (CH_3), 17.0 (CH_3), 23.3 (CH_3), 50.4 (CH_3), 50.6 (CH_3), 54.7 (CH), 58.3 (C), 93.1 (C), 108.7 (C), 117.7 (CH), 118.8 (CH), 119.5 (CH), 133.7 (C), 136.1 (C), 140.5 (C), 144.9 (C), 145.8 (C), 148.1 (C), 153.1 (C). **9**: ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H), 2.07 (d *J*=1.2 Hz, 3H), 2.12 (s, 3H), 2.40 (d, *J*=0.8 Hz, 3H), 2.42 (br s, 3H), 5.96 (q', *J*=1.5 Hz, 1H), 6.37 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.50 (CH_3), 15.54 (CH_3), 17.2 (CH_3), 20.7 (CH_3), 24.7 (CH_3), 118.3 (CH), 125.3 (CH), 126.6 (CH), 129.1 (C), 132.8 (C), 133.6 (C), 136.7 (C), 136.8 (C), 137.5 (C), 137.7 (C), 140.4 (C), 142.3 (C), 142.8 (C), 143.4 (C), 168.7 (C). **10**: ^{1}H NMR ($CDCl_3$) δ 1.71 (d, *J*=7.2 Hz, 3H), 2.35 (d, *J*=0.6 Hz, 3H), 2.43 (s, 3H), 2.45 (d, *J*=0.7 Hz, 3H), 4.24 (q, *J*=7.0 Hz, 1H), 6.74 (s, 1H), 7.16 (q', *J*=0.8 Hz, 1H), 7.47 (q', *J*=0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.01 (CH_3), 15.04 (CH_3), 15.6 (CH_3), 18.2 (CH_3), 33.0 (CH), 122.6 (CH), 127.5 (C), 128.9 (CH), 130.6 (CH), 134.8 (C), 137.6 (C), 138.1 (C), 138.8 (C), 139.3 (C), 142.3 (C), 145.8 (C), 155.1 (C), 181.2 (C).

8) K. E. Richards, R. W. Tillman, and G. J. Wright, *Aust. J. Chem.*, **28**, 1289 (1975).

9) C. Wesdemiotis and F. W. McLafferty, *J. Am. Chem. Soc.*, **109**, 4760 (1987); B. J. Smith, M. T. Nguyen, W. J. Bouma, and L. Radom, *ibid.*, **113**, 6452 (1991).

10) Irradiation of **1a** in ethanol by a low-pressure mercury lamp gave an aldehyde **13** in 8% yield together with **4** (34%), which strongly suggests the generation of the carbene **14**. Moreover, irradiation of **3c** under similar conditions also gave **13** in 7% yield. Details about the photolysis of **1** with a low-pressure mercury lamp will be reported elsewhere.



13 : X= -CHO
14 : X= -$\ddot{C}$-OH

11) R. M. Moriarty and C.-L.Yeh, *Tetrahedron Lett.*, **1972**, 383.

12) R. K. Russell, R. E. Wingard, Jr., and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 7483 (1974); L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, **1973**, 1713; H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Am. Chem. Soc.*, **90**, 6096 (1968); H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

13) R. Hoffmann, *Tetrahedron Lett.*, **1970**, 2907; H. Günther, *ibid.*, **1970**, 5173; R. Hoffmann and W.-D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941 (1971).

14) S. Rajappa, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Cheeseman, Pergamon Press, Oxford (1984), Vol. 4, p. 779.

(Received December 18, 1992)