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# Substituent effects on di-π-methane and aza-di-π-methane rearrangements of dibenzo[*f*,*h*]quinoxalinobarrelenes

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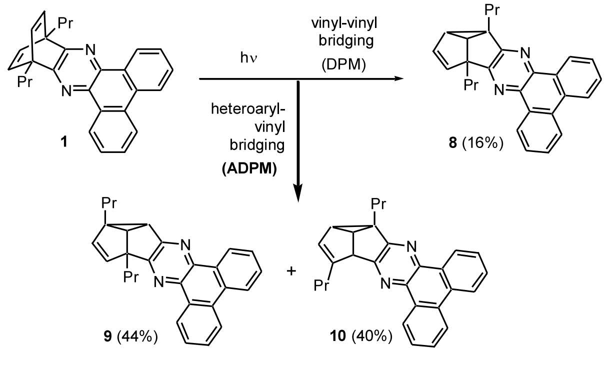
**Abstract**—The photochemical isomerizations of the title barrelenes providing the corresponding semibullvalenes are described. The modes of competitive di-π-methane and aza-di-π-methane rearrangements depend on the substitutions on the heterobarrelenes.

The di-π-methane rearrangement (Zimmerman rearrangement), owing to its importance in organic synthesis as well as its interesting mechanistic aspects, has attracted much attention from the organic community.[1] Photochemical studies of bicyclic systems that contain more than one di-π-methane chromophore can provide more information about the properties of excited state molecules. There has been continued interest in recent years to evaluate the factors that control the di-π-methane photorearrangements in bicyclic systems.[1–3] In this aspect, the photochemical investigations of arene- and heteroarene-fused barrelenes have been carried out to address the issues related to chemo- and regio-selective outcome.[1c,2,4,5] In our laboratory, the photochemistry of pyrazino- and quinoxalino-fused barrelenes has been studied.[4] Most of these heteroaromatic barrelenes underwent predominantly aza-di-π-methane (ADPM) rearrangement[6] rather than di-π-methane (DPM) rearrangement. In continuation of our studies, we carried out the photochemistry of dibenzo[*f*,*h*]quinoxalinobarrelenes with the main aim of examining the competing aptitude of DPM and ADPM modes. Herein we report the synthesis and photochemical rearrangements of title barrelenes **1**–**3**.

The barrelenes **1**–**3**[†] were synthesized by the condensation of diaminophenanthrene (**4**) with α-diketones **5**–**7**,[4a,7] respectively (Fig. 1). Direct irradiation of barrelene **1** in benzene using light of wavelength centered at 350 nm in a Rayonet reactor for about 10 h furnished semibullvalenes **8**–**10**[8] in 16:44:40 ratio,[9] respectively[‡] (Scheme 1). While the minor DPM product **8** resulted from the initial vinyl–vinyl bridging, the major ADPM products **9** and **10** were formed in equal amounts via initial heteroaryl-vinyl bridging. Similar results were obtained when the reaction was performed in cyclohexane, methanol or acetone.

In contrast to the reaction of **1**, the irradiation of diester-substituted heterobarrelene **2** in cyclohexane



**Scheme 1.**

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[†] All new compounds were characterized by IR, $^1$H and $^{13}$C NMR, DEPT, and low and high resolution MS analyses; the majority of the compounds provided satisfactory elemental analysis.

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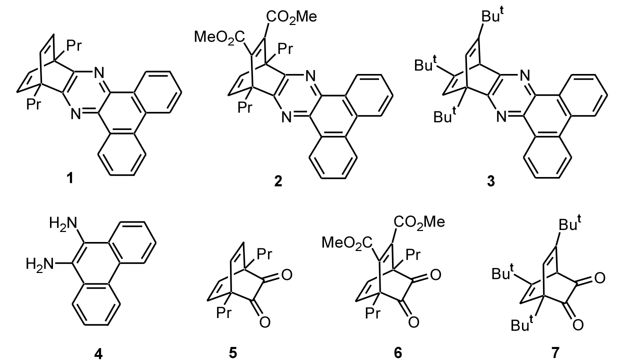
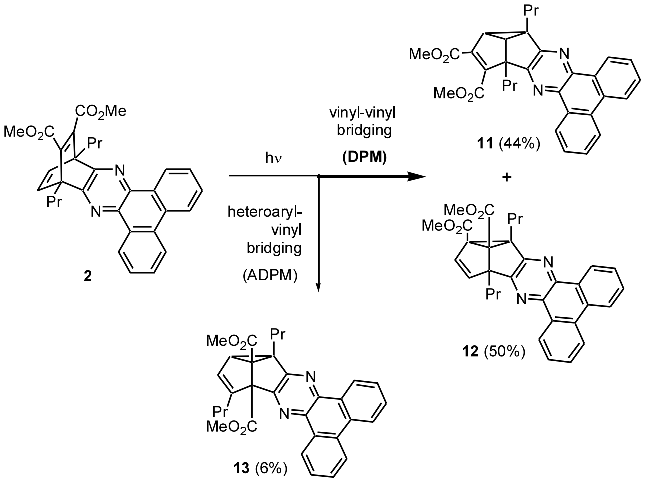
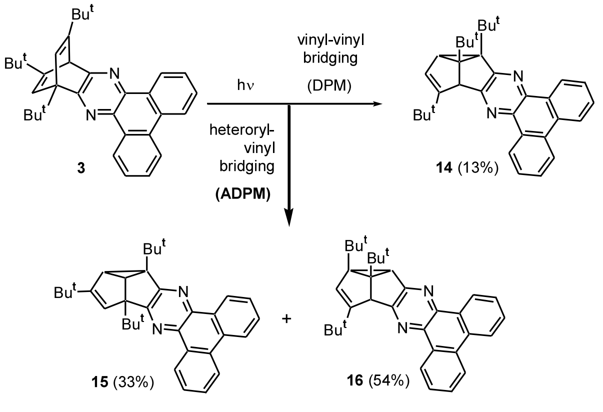


**Figure 1.**



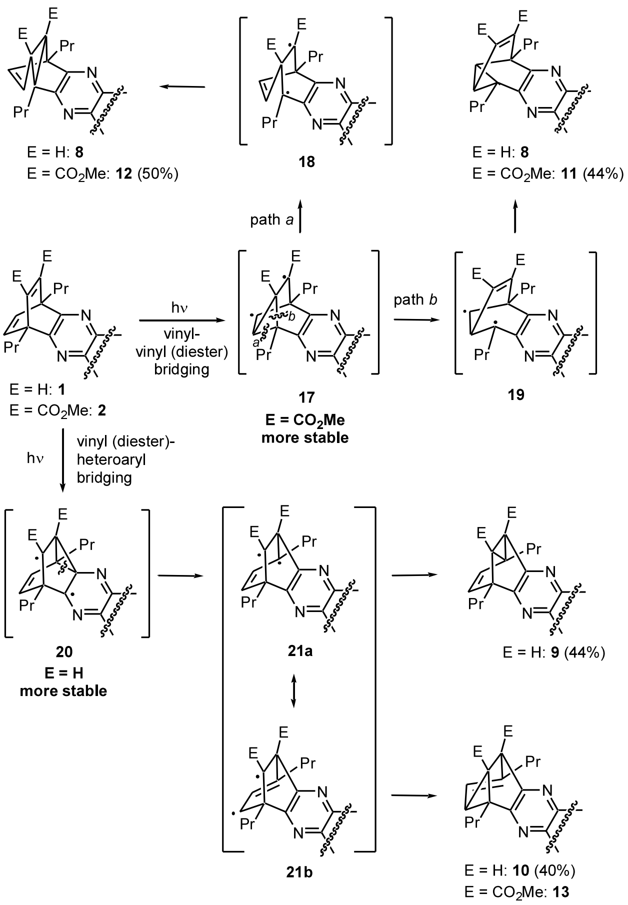
**Scheme 2.**



**Scheme 3.**

using light of wavelength centered at 350 nm for 6 h proceeded predominantly through DPM pathway to produce semibullvalenes **11** and **12** in 44:50 ratio[8,9] (Scheme 2). A minor (6%) photoisomer **13** was obtained through ADPM process.[‡]

Direct irradiation of barrelene **3** in benzene (350 nm, 2.5 h) provided DPM product **14** and ADPM products **15**[10] and **16** in 13:33:54 ratio,[8,9] respectively (Scheme 3). Here the product obtained via DPM process is minor and those obtained via ADPM process are major.



**Scheme 4.**

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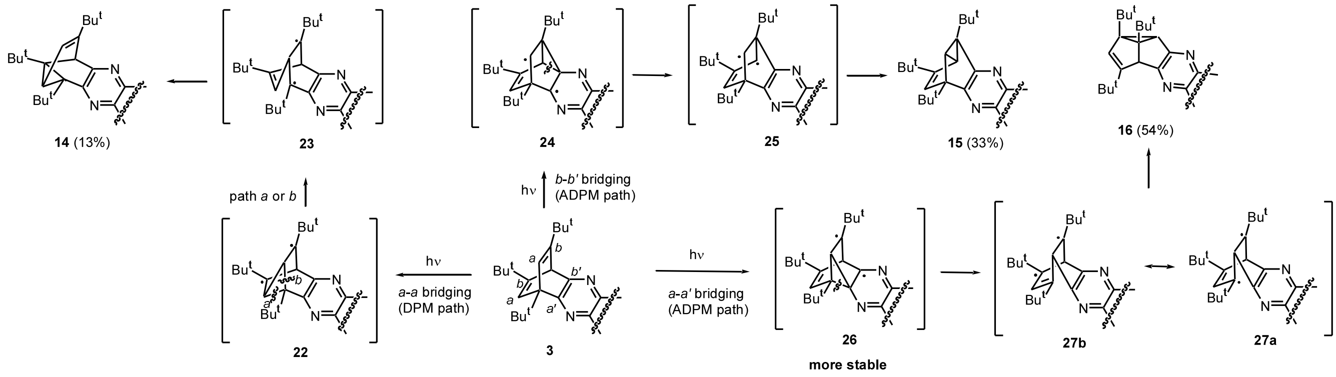
[‡] Spectroscopic data for representative products. **9**: $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.95 (t, $J$=7.3 Hz, 3H), 0.99 (t, $J$=7.3 Hz, 3H), 1.40–1.61 (m, 5H), 1.94–2.03 (m, 2H), 2.24–2.29 (m, 1H), 2.95 and 3.14 (ABq, $J$=6.2 Hz, 2H), 5.16 and 5.47 (ABq, $J$=5.0 Hz, 2H), 7.59–7.64 (m, 4H), 8.51–8.52 (m, 2H), 9.15–9.20 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 14.3, 14.8, 19.0, 21.4, 33.1, 36.2, 40.2, 54.3, 54.3, 64.2, 122.5, 122.5, 124.8, 124.9, 126.5, 127.1, 127.2, 128.9, 128.2, 130.3, 130.5, 130.5, 130.7, 136.2, 137.4, 138.7, 153.9, 163.0. **12**. $^1$H NMR (CDCl$_3$, 400 MHz): δ 1.02 (t, $J$=7.3 Hz, 3H), 1.12 (t, $J$=7.3 Hz, 3H), 1.37–1.66 (m, 2H), 2.33–2.59 (m, 4H), 3.82 (s, 3H), 3.85 (s, 3H), 5.60 and 5.70 (ABq, $J$=5.2 Hz, 2H), 7.77–8.57 (m, 4H), 8.60–8.62 (m, 2H), 9.21–9.25 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 15.0, 18.7, 21.4, 28.5, 31.2, 52.0, 52.6, 55.9, 58.7, 67.4, 67.5, 122.6, 127.4, 127.5, 128.8, 128.9, 130.2, 130.2, 130.7, 131.1, 138.8, 138.9, 139.7, 151.4, 161.0, 166.6, 168.6. **16**. $^1$H NMR (CDCl$_3$, 400 MHz): δ 1.08 (s, 9H), 1.18 (s, 9H), 1.32 (s, 9H), 3.40 (s, 1H), 4.45 (s, 1H), 5.44 (s, 1H), 7.69–7.72 (m, 4H), 8.60–8.63 (m, 2H), 9.19–9.29 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 29.5, 30.8, 31.0, 33.7, 33.9, 34.0, 39.1, 60.4, 63.7, 78.4, 122.6, 122.6, 123.8, 124.8, 127.2, 128.0, 128.2, 130.4, 130.6, 130.9, 136.4, 138.7, 154.9, 156.5, 162.7.



**Scheme 5.**

The change in the pathways (DPM versus ADPM) in the reactions of barrelenes **1** and **2** is thought to result from the stabilities of the biradical species generated after the initial bridging. A plausible reaction mechanism is depicted in Scheme 4. In the case of barrelene **1**, the biradical **20** (E = H) leading to ADPM products **9** and **10** is more stabilized by the dibenzo[*f*,*h*]quinoxalino ring through a significant degree of delocalization of spin density from carbon to neighboring nitrogen atom, though the aromaticity of the heteroaromatic ring is partially broken. The biradical **20** (E = H), being a tertiary radical, is profoundly stabilized over the biradical **17** (E = H), which is a secondary radical. On the contrary, in the reaction of barrelene **2**, the biradical **17** (E = $CO_2Me$) leading to DPM products **11** and **12** is more stabilized by the ester group without desrupting the aromaticity of the heteroaromatic ring. Furthermore, the formation of **12** is noticeably higher than that of **11** due to the relatively higher stability of **18** over **19** (E = $CO_2Me$) as a result of the polar nature and radical-stabilizing ability of ester group[11] at the radical center of **18**.

A plausible reaction mechanism for the formation of photoproducts **14**–**16** from barrelene **3** is outlined in Scheme 5. The DPM product **14** was formed through initial *a*–*a* bond formation to biradical species **22**. The cleavage of either bond *a* or bond *b* of **22** generates symmetrical species **23**; then ring closure occurs to give semibullvalene **14**. The initial *b*–*b*′ bridging and *a*–*a*′ bridging generate biradical species **24** and **26** leading to the formation of ADPM products **15** and **16**, respectively. However, ADPM pathways (initial *a*–*a*′ and *b*–*b*′ bridging) are predominated over DPM pathway (initial *a*–*a* bridging) resulting from the stabilities of the biradical species generated. Furthermore, owing to the steric reasons, *a*–*a*′ bridging is more facile over initial *b*–*b*′ bridging and hence the formation of **16** is greater than that of **15**.

In conclusion, we presented the photochemical reactions of a new class of heteroarene-fused barrelenes. The barrelenes **1** and **3** without ester functionalities on the vinylic bond proceeded photochemical isomerizations to afford ADPM products predominantly. On the other hand, the barrelene **2** bearing strong electron-withdrawing ester groups on vinylic bond underwent photolysis to produce DPM products predominantly. The relative stability of the biradical species dictates the initial bridging and the product distribution as well.

## Acknowledgements

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