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Substituent effect on regioselectivity in the di-π-methane rearrangement: synthesis of disubstituted benzobarrelene derivatives and their photochemistry

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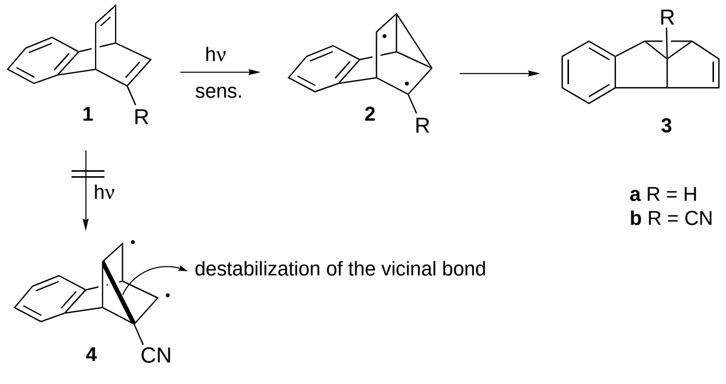
Abstract—2,3- and 2,5-Dicyanobenzobarrelenes **5** and **6** have been synthesized and subjected to triplet-sensitized photoisomerization. 2,3-Dicyanobenzobarrelene **5** gave two di-π-methane rearrangement products **7** and **8** and a [2π+2π]-cycloaddition product **9**. However, 2,5-dicyanobenzobarrelene **6** formed a single di-π-methane product **13**. The formation of these products is discussed in terms of the radical stabilizing effect of the substituents and the destabilizing effect on the formation of the cyclopropane ring. © 2001 Elsevier Science Ltd. All rights reserved.

The di-π-methane rearrangement has attracted much attention from organic chemists because of its importance in organic synthesis as well as its interesting mechanistic aspects.[1] The photolysis of benzobarrelene **1a** affords benzosemibullvalene **3a** (Scheme 1). The semibulvalenes are known to arise from the triplet excited state through a di-π-methane rearrangement and the vinyl–vinyl bridging is the main pathway in the photorearrangement of benzobarrelenes. Introduction of the substituents on the vinyl group destroys the symmetry of the benzobarrelene skeleton increasing the number of possible initial bonding modes. Nevertheless, the reaction generally shows great site- and regio-selectivity. The effect of one or two substituents on the bridging and regioselectivity of the di-π-methane rearrangement has been investigated by Bender,[2] Paquette,[3] Hemmetsberger,[4] Scheffer[5] and George et al.[6] intensively.

For example, the sensitized di-π-methane rearrangement of cyanobenzobarrelene **1b** (R = CN) furnishes only benzosemibullvalene **3b**.[3,7] Mechanistic studies have revealed that this reaction proceeds via vinyl–vinyl bridging between the less substituted carbon atoms because of the favorable stabilization of the diradical intermediate **2b** by the cyano group. However, the destabilization[8] of the intermediate **4** by the substituent has not been considered. In a recent study, we have shown that the destabilization of the cyclopropane ring



Scheme 1.

Keywords: di-π-methane rearrangement; benzobarrelene.

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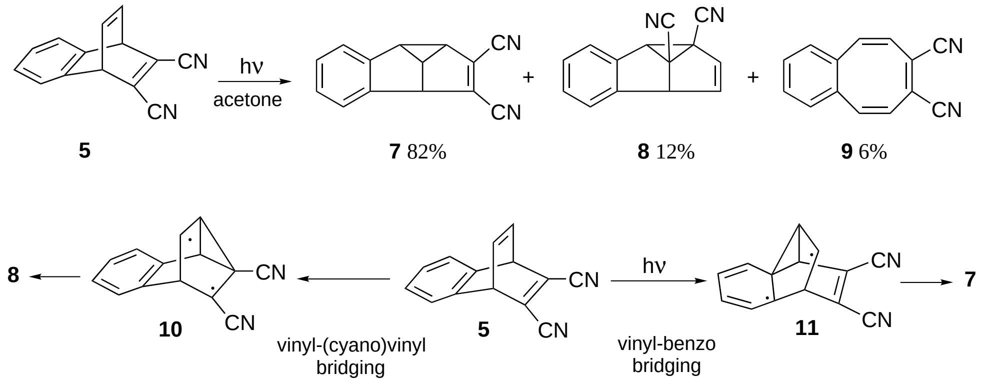
plays an important role in determining the mode of the reaction as much as the stabilization effect of the diradical intermediates.[9] In this communication, we describe further experiments, which support the view that destabilization of the cyclopropane ring determines the mode of the di-π-methane rearrangements.

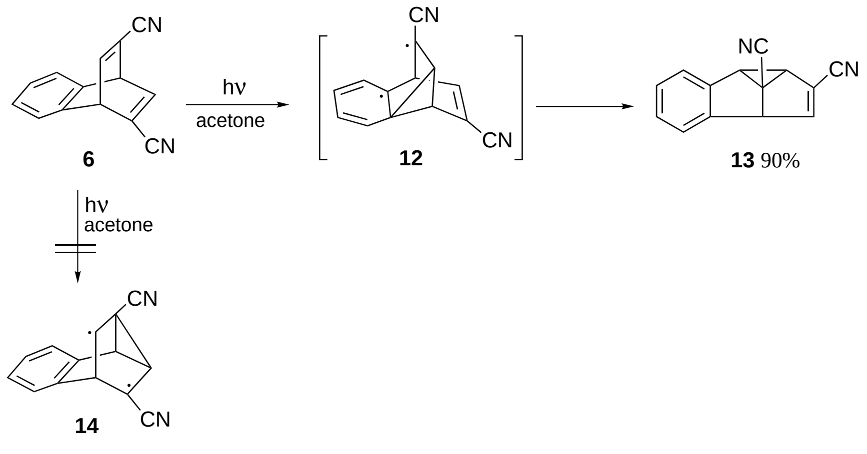
For that reason, we have synthesized dicyanobenzobarrelene derivatives **5** and **6** starting from the corresponding dibromobenzobarrelenes.[9] Dibromobenzobarrelenes were allowed to react with cuprous cyanide in dimethylformamide under reflux for 22 h. The substitution products **5** and **6** were isolated in 60 and 19% yields, respectively. Our interest lay primarily in the triplet-sensitized photochemistry of **5** and **6**. Photochemical reactions were conducted in acetone solution. The apparatus consisted of a 254 nm mercury arc lamp surrounded by a water-cooled quartz immersion vessel.

Irradiation of **5** in acetone gave a mixture of three photoproducts **7**, **8**, and **9** (82, 12, and 6%), respectively (Scheme 2). The products were separated by column chromatography. The structures have been elucidated on the basis of the spectral data obtained by ^{1}H (400 MHz), ^{13}C NMR and mass spectral measurements.[10] Irradiation of **6**, similarly gave the isomer **13** regiospecifically in 90% yield (Scheme 3). The structure was confirmed again by the spectral data.[11] The cyclopropane protons appear as an AB-system ($J_{AB}=7.4$ Hz) at 3.6 and 3.8 ppm. The olefinic proton resonance appears at 6.2 ppm as a doublet ($J=2.7$ Hz) coupled to the adjacent methine proton. Furthermore, the methine proton appears as a doublet ($J=2.7$ Hz) which is in accordance with the suggested structure.

Photolysis of **5** gave two different di-π-methane rearrangement products **7** and **8**. The major product **7** (82%) can be formed only by vinyl–benzo bridging (**11**) (Scheme 2). Zimmerman et al.[1e] have proved by labeling experiments that vinyl–vinyl bridging is the major process for the transformation of benzobarrelene to benzosemibullvalene systems. However, contrary to the finding of Zimmerman et al., the major product **7** is formed via benzo–vinyl bridging. This can be explained by the destabilization effect of the adjacent bond in an initially formed cyclopropane ring in **10**. The minor product **8** can be formed only by vinyl–vinyl bridging. The formation of this product indicates that the vinyl–vinyl bridging is not completely suppressed. We assume that the destabilization effect of the cyclopropane ring by the cyano group overwhelms the radical stabilization effect of cyano group. In a case, where both effects are operating, the destabilization effect of the cyano group

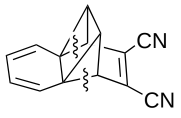


Scheme 2.



Scheme 3.

on the cyclopropane ring determines the mode of the di-π-methane rearrangement. For the formation of **9** there are three possible modes of the initial $[2_\pi+2_\pi]$-cycloadditions: (i) benzo–vinyl, (ii) benzo–(cyano)vinyl and (iii) vinyl–(cyano)vinyl cycloadditions. We propose the intermediate **15** is formed initially, followed by a retro-cycloaddition to give **9**.



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The formation of the product **13** isolated from the irradiation of **6** can be attributed to the initial formation of the cyclopropane intermediate **12** which is the result of vinyl–benzo bridging (Scheme 3). In the case of **6**, the initial formation of an intermediate **14** resulting from vinyl–vinyl bridging is completely suppressed. The sole formation of **13** strongly supports our suggestion that the cyano groups prevents the formation of the intermediate **14** where a cyano group is directly attached to the cyclopropane ring.

In conclusion: in di-π-methane rearrangements, the destabilizing effect of the electron-withdrawing substituents on the initially formed cyclopropane ring plays the dominating role in determining the mode of the rearrangements.

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11. Spectral data: compound **7**: white crystals, mp: 150–151°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.5–7.2 (m, 4H), 4.1 (d, $J=6.5$ Hz, 1H), 3.6 (q, $J=6.5$ Hz, 1H), 3.5 (t, $J=6.5$ Hz, 1H), 3.1 (t, $J=6.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.5, 144.5, 136.6, 135.7, 133.8, 129.8, 125.3, 120.2, 119.6, 63.9, 56.6, 49.3, 47.4; MS (m/z): 204 (M$^+$, 88%), 203 (100%), 176 (M$^+$–CN, 40%), 148 (M$^+$–2CN, 17%). Compound **8**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.2–7.0 (m, 4H), 5.8 (dd, $J=5.4$ and 2.5 Hz, 1H), 5.15 (d, $J=5.4$ Hz, 1H), 4.32 (d, $J=2.5$ Hz, 1H), 4.1 (s, 1H); MS (m/z): 204 (M$^+$, 88%), 203 (100%), 176 (M$^+$–CN, 40%), 148 (M$^+$–2CN, 17%). Compound **9**: pale yellow crystals, mp: 162–163°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.5–7.2 (m, 4H), 6.9 (d, $J=11.7$ Hz, 2H), 6.1 (d, $J=11.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.7, 133.0, 128.8, 127.6, 125.4, 124.6, 113.9; MS (m/z): 204 (M$^+$, 100%), 176 (M$^+$–CN, 41%), 148 (M$^+$–2CN, 7%). Compound **13**: white crystals, mp: 155–156°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.5–7.2 (m, 4H), 6.27 (d, $J=2.6$ Hz, 1H), 4.1 (d, $J=2.6$ Hz, 1H), 3.8 (d, $J=7.4$ Hz, 1H), 3.6 (d, $J=7.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.5, 146.1, 134.7, 129.6, 127.6, 127.57, 124.0, 118.7, 115.6, 114.4, 56.0, 44.6, 42.4, 40.0; MS (m/z): 204 (M$^+$, 90%), 203 (100%), 177 (35%), 176 (M$^+$–CN, 20%), 148 (M$^+$–2CN, 15%).