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Photochemical di-π-methane rearrangement of quinoxalinobarrelenes

Vijay Nair [a,*], Gopinathan Anilkumar [a], Jaya Prabhakaran [a], Davis Maliakal [a],
Guenter K. Eigendorf [b], Paul G. Williard [c]

[a] *Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India*
[b] *Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Z1*
[c] *Department of Chemistry, Brown University, Providence, RI 02912, USA*

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Abstract

Quinoxalinobarrelene **1** underwent facile di-π-methane rearrangement when irradiated in cyclohexane at 250 nm to afford quinoxalinosemibullvalene **2** in 94% yield. Similar rearrangement was observed with **3** leading to the corresponding semibullvalene **4**. © 1997 Elsevier Science S.A.

Keywords: Quinoxalinobarrelene; Di-π-methane rearrangement; Quinoxalinosemibullvalene

1. Introduction

The photochemical di-π-methane rearrangement (Zimmermann rearrangement) of barrelenes [1–3] and their benzo [4] and dibenzo [5–7] analogs has been the subject of extensive investigations. In contrast, however, the photochemistry of azaheterocyclic analogs of benzobarrelenes has received very little attention; the di-π-methane rearrangement of pyrazinobarrelenes [8,9] and quinoxalinobarrelenes [10] reported by Liao et al. and Liao and Yang constitute the only investigations in this area.[1]

In the context of our recent work [12–14] on the synthesis and reactions of bicyclo[2.2.2]octene-7,8-diones and the facile conversion of the latter to the corresponding quinoxalinobarrelenes, it was of interest to study their photochemistry [15]. The results obtained on irradiating representative compounds are reported here.

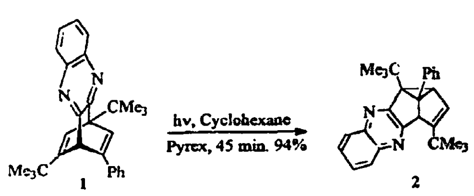
2. Results and discussion

Quinoxalinobarrelene **1**, readily obtained from the cycloadduct of 3,5-di-*tert*-butyl-*o*-benzoquinone and phenylacetylene [15,16] on irradiation in cyclohexane using a 450 W medium pressure mercury vapour lamp for 45 min afforded the crystalline product **2** in 94% yield, presumably via a di-π-methane rearrangement (Scheme 1).

The structure of **2** was discerned from its spectral and analytical data. In the ^1H NMR spectrum of **2**, the proton on the cyclopropane resonated as a doublet ($J = 2.7$ Hz) at δ 3.45. The olefinic proton adjacent to the *tert*-butyl group also appeared as a doublet ($J = 2.7$ Hz) at δ 5.41. The proton at the ring junction exhibited a singlet at δ 4.23. The structure was further supported by the presence of a molecular ion peak at m/z 394 in the mass spectrum. Final proof for the structure was obtained by single crystal X-ray analysis [Williard, unpublished results].

Quinoxalinobarrelene **3**, the regioisomer of **1**, when subjected to photolysis under the same conditions afforded the product **4** in 66% yield (Scheme 2).

The course of the rearrangement may be rationalized on the basis of the stability of the intermediate diradical; an illustration is provided by the formation of **2** (Scheme 3). It is worthy of note that in all the three cases studied, only vinyl–vinyl bridging product was obtained, whereas vinyl–vinyl and pyrazino–vinyl bridging products were obtained by Liao et al. [8] and Liao and Yang [9,10]. Although we have not



Scheme 1.

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* Corresponding author.

[1] For a review on aza di-π-methane rearrangement, see Ref. [11].

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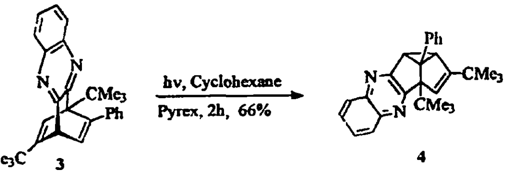
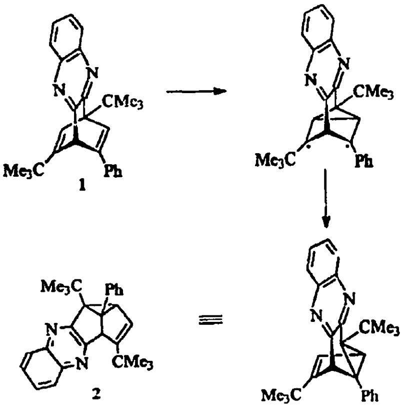


Scheme 2.



Scheme 3.

conducted any mechanistic investigations, it may be surmised that in analogy with Liao et al.'s [8] observations, the rearrangement described occurs via the triplet state (n, π^* or π, π^*) of the quinoxalinobarrelene. It is worthy of note that although the transformation of **1** to **2** occurs by a di-π-methane rearrangement, the product **4** can be formed from **3** either via di-π-methane or aza di-π-methane rearrangement.

Attempts to obtain additional information on the nature of the excited state involved in the rearrangement have not been fruitful. Sensitizers such as acetophenone and benzophenone were not useful due to their absorption in the region 300–360 nm where **3** also absorbs. No reaction was observed when benzil was used as the sensitizer, presumably due to its triplet energy being lower than that of **3**. Irradiation of **3** in acetone gave a mixture of products from which **4** was isolated in 40% yield.

In conclusion, we have observed a facile photochemical rearrangement of quinoxalinobarrelenes to the corresponding semibullvalenes, presumably via a di-π-methane pathway.

3. Experimental

Melting points were recorded on a Toshniwal capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 882 spectrophotometer. NMR spectra were run on a JEOL EX-90 or Bruker 200 MHz NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on a Hewlett Packard 5970 mass selective detector.

3.1. *Quinoxalinosemibullvalene 2*

A degassed solution of quinoxalinobarrelene **1** (320 mg, 0.81 mmol) in cyclohexane (250 ml) was irradiated in a Pyrex filter using a 450 W Hanovia mercury lamp for 45 min. The solvent was removed in vacuo and the crude product was subjected to chromatography on silica gel using 2% EtOAc in hexane as the eluent to afford the product **2** (300 mg, 94%) as colourless crystals; recrystallized from hexane. M.p. 133–134°C: IR (KBr): 2957, 2903, 1353 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.12 (9H, s), 3.46 (1H, d, $J=2.7$ Hz), 4.24 (1H, s), 5.44 (1H, d, $J=2.7$ Hz), 7.21–7.38 (5H, m), 7.55–7.72 (2H, m), 7.91–8.10 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 28.64, 30.87, 33.38, 34.66, 42.03, 58.14, 62.44, 70.32, 119.57, 127.36, 127.93, 128.05, 128.26, 128.55, 128.88, 133.82, 139.17, 141.29, 158.45, 162.98; EIMS *m/z* (relative intensity): 394 (M^+, 23), 379 (38), 337 (85), 323 (100), 281 (90), 57 (39).

3.2. *Quinoxalinosemibullvalene 4*

Colourless crystals (165 mg from 250 mg of **3**, 66%), recrystallized from hexane. M.p. 142–143°C: IR (KBr): 2967, 2880, 1568, 1486 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.18 (9H, s), 1.20 (9H, s), 3.21–3.46 (2H, m), 5.49 (1H, s), 6.97–7.38 (5H, m), 7.60–7.76 (2H, m), 7.96–8.17 (2H, m): ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 27.68, 27.86, 28.67, 31.95, 35.47, 35.59, 52.30, 58.26, 72.73, 126.88, 127.39, 127.66, 127.99, 128.38, 128.94, 129.33, 129.60, 132.52, 147.74, 158.12, 165.34; EIMS *m/z* (relative intensity): 394 (M^+, 12), 338 (15), 323 (28), 281 (100), 57 (23). Anal. Calcd. for $C_{28}H_{30}N_2$: C, 85.2; H, 7.36; N, 7.10. Found: C, 84.74; H, 7.75; N, 7.63.

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