Synthesis and photochemical transformations of a few olefin-appended 11,12-dibenzoyldibenzobarrelenes

Ambily Mary Jacob[a], Gisha George[a], Jomon P. Jacob[a] and Eason M. Mathew[b*]

[a]*Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-682 022, Kerala, India*

[b]*Research and Development Division, Arjuna Natural Extracts Ltd., Aluva-683101, Kerala, India*

Several olefin-appended dibenzobarrelenes have been synthesised by Diels–Alder reaction between 9-alkenylanthracenes and dibenzoylacetylene under carefully controlled conditions and their photochemistry was examined. Olefin appendages acted as efficient quenchers of the triplet state of these barrelenes.

Keywords: Diels–Alder reaction, dibenzobarrelenes, intramolecular quenching, di-π-methane rearrangement, dibenzocyclooctatetraene, dibenzosemibullvalene

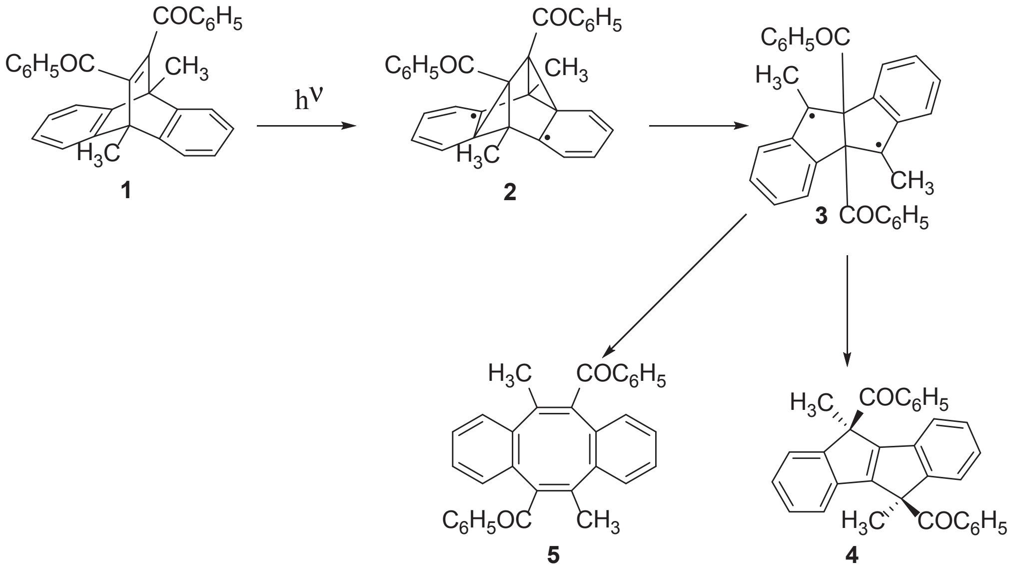
Photochemistry of barrelene derivatives has attracted considerable attention.[1-11] Their ability to undergo singlet mediated electrocyclic reactions and triplet mediated di-π-methane and tri-π-methane rearrangements make them attractive substrates for mechanistic investigations.[2,12-14] Over the past few decades, several barrelene derivatives were synthesised and their photochemistry was examined in great detail. Upon irradiation, barrelenes give the corresponding cyclooctatetraenes and/or semibullvalene derivatives.[15] In most cases, both singlet mediated cyclooctatetraene generation and triplet mediated di-π- and tri-π-methane rearranged products are concurrently generated.[15,16] This is due to competing intersystem crossings under direct irradiation conditions and partial absorption of light by barrelenes under triplet sensitised irradiation conditions.

The nature of substituents plays an important role in barrelene photochemistry. George *et al.*[15,17-20] have established that benzoyl groups at 11,12-postions of dibenzobarrelenes promote intersystem crossing resulting in preferential generation of triplet mediated products even under direct irradiation. They examined the photochemistry of several 11,12-dibenzoyldibenzobarrelenes having a variety of substituents at the 9- and 10-positions **1**.[15,21] Depending on the nature of the 9,10-substituents, either 4b- or 8b-substituted semibullvalenes (or products derived thereof) were formed in major amounts. In the case of dibenzobarrelene **1**, tri-π-methane rearrangement leading to 1,4-diradical intermediates **2**, **3** gave a mixture of dibenzopentalene **4** and cyclooctatetraene **5** derivatives (Scheme 1).[13,15]

Interestingly, the role of olefinic substituents on barrelene photochemistry remains unexplored. In this context, we wished to synthesise a few 11,12-dibenzoyldibenzobarrlenes having olefin appendages at the 9-position. Olefins are known triplet quenchers.[22,23] Intramolecular quenching is expected to be more efficient than intermolecular quenching. We reasoned that efficient intramolecular quenching of the triplet excited states by the olefin appendage will enable the emergence of alternative reaction pathways for these barrelenes. We now describe our efforts to divert the photochemistry of systems that are known to undergo triplet mediated pathways to other reaction possibilities.

Results and discussion

Several olefin appended dibenzobarrelenes **8a–c** were synthesised by the Diels–Alder reaction of olefin appended anthracene derivatives **6a–c** with dibenzoylacetylene (**7**) (Scheme 2). 9-Alkenylanthracenes **6a–c** were synthesised by employing the Wittig reaction, Grignard reaction and Claisen–



Scheme 1

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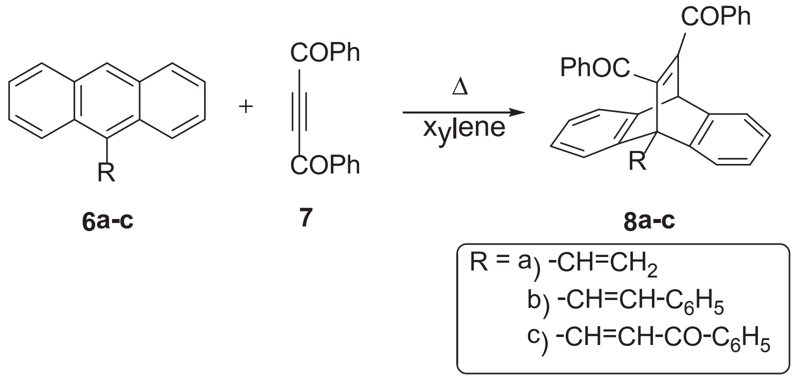
* Correspondent. E-mail: easonmmathew@gmail.com



Scheme 2

Schmidt reaction. Note that introduction of a vinyl substituent at the bridgehead position of dibenzobarrelenes offers two distinct possibilities: (1) generation of a tetra-π-methane system capable of exhibiting interesting photochemistry; and (2) generation of dibenzobarrelenes where intramolecular triplet quenching is a distinct possibility.

Photochemistry of 11,12-dibenzoyldibenzobarrelenes (**8a–c**)

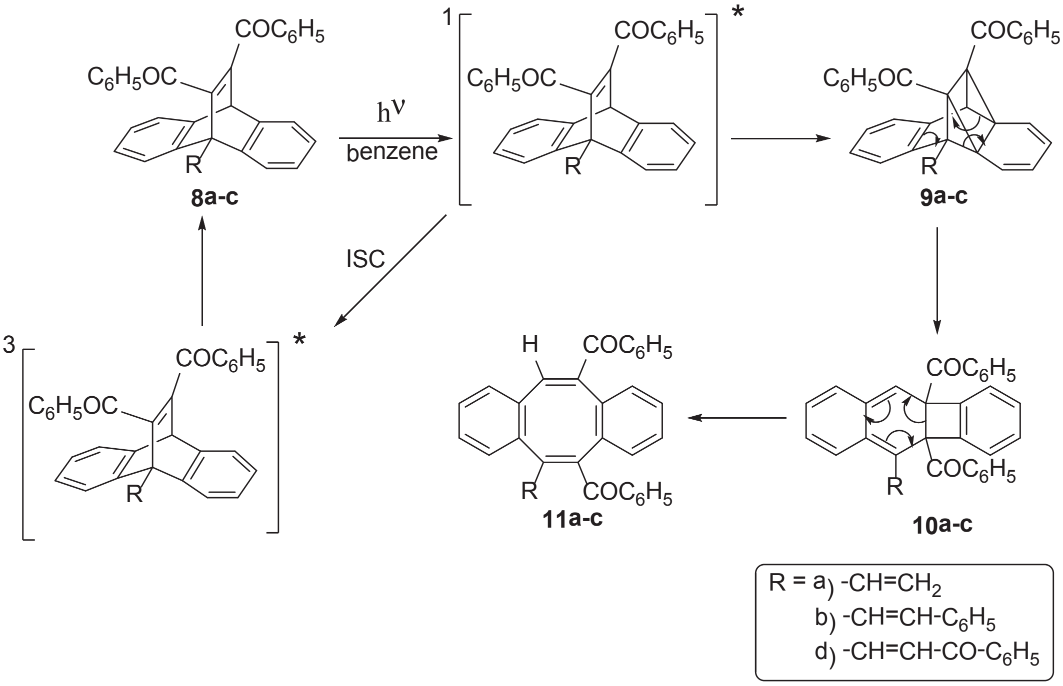
All irradiation experiments were performed using a Rayonet photochemical reactor employing 300 nm lamps. Irradiation of **8a** in benzene (8 mM) for 30 minutes resulted in near-quantitative recovery of unchanged starting material. However, prolonged irradiation (10h) of **8a** in benzene (8 mM) at 300 nm gave the dibenzocyclooctatetraene **11a** as the only photoproduct. The structural identity of the photoproduct **11a** was established on the basis of spectral and analytical data.

Similar behaviour was exhibited by dibenzobarrelenes **8b** and **8c.** Irradiation of **8b** and **8c** in benzene (8 mM) at 300 nm resulted in the formation of the dibenzocyclooctatetraene **11b** and **11c** respectively. Here also there was no trace of dibenzosemibullvalenes, indicating efficient intramolecular quenching of the triplet excited states of the dibenzobarrelenes by the olefin appendage at their bridgehead position. The following mechanism is proposed for the photochemical outcome (Scheme 3). It may be noted that formation of dibenzocyclooctatetraene is observed only upon prolonged irradiation. We conclude that all barrelene triplets are quenched by the olefin appendage leaving the singlet excited state to react. Since intersystem crossing is efficient here, the singlet excited state is present only as a minor fraction and hence generation of the singlet mediated dibenzocyclooctatetrene is at a very slow rate.

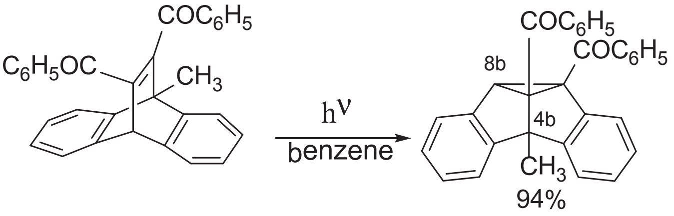
Typically, 11,12-dibenzoyldibenzobarrelenes undergo efficient intersystem crossing leading to triplet-mediated products such as dibenzosemibullvalenes. In a control experiment, irradiation of 9-methyl-11,12-dibenzoyldibenzobarrelene (**12**) under identical conditions (0.8 mmol in benzene at 300 nm) gave the corresponding 4b-substituted semibullvalene (**13**) in near-quantitative amounts in 30 minutes (Scheme 4).[18] This control experiment revealed that irradiation conditions applied by us are appropriate for barrelene–semibullvalene rearrangement to manifest itself in systems where the intramolecular quenching possibility is nonexistent. Hence intramolecular quenching and diversion of barrelene photochemistry is facilitated by the olefin appendages present in them.

Conclusion

We have examined the photochemistry of a few representative olefin-appended dibenzobarrelenes. Olefin appendages act



Scheme 3



12 **13**

Scheme 4

as efficient triplet quenchers resulting in slow but exclusive generation of singlet mediated products.

Experimental

All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by TLC. Aluminium sheets coated with silica (Merck) were used for TLC. Visualisation was achieved by exposure to iodine vapour or UV radiation. Column chromatography was carried out with slurry-packed silica (Qualigens 60–120 mesh). All steady state irradiations were carried out using a Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. Absorption spectra were recorded using a Shimadzu 160A spectrometer and IR spectra were recorded using a ABB Bomem (MB series) FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz on a Bruker FTNMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of TMS. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 using argon/xenon as the FAB gas, at Central Drug Research Institute (CDRI), Lucknow. Elemental analysis was performed on Elementar Systeme (Vario ELIII) at the Sophisticated Test and Instrumentation Centre (STIC), Kochi.

*Synthesis of 9-olefin appended anthracenes (**6a–c**); general procedure*

9-Vinylanthracene (**6a**): [24] *(a) Wittig reaction*: A solution of 9-anthraldehyde (4.12 g, 0.02 mol) in dry THF (80 mL), was added to the stirred mixture of methyltriphenylphosphonium iodide (24.24 g, 0.06 mol) in dry THF (120 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5h. An aqueous solution of NaOH (50%), was then added from a dropping funnel. The reaction mixture was stirred for another 30 min, poured into water and extracted with dichloromethane. The organic layer was separated, washed with water and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the product mixture was separated by column chromatography and purified by recrystallisation from a mixture of hexane and dichloromethane (3:2) to give **6a** in pure form.

(b) Grignard reaction: A solution of anthrone (15.0 g, 0.08 mol) dissolved in dry THF (200 mL), was added to a mixture of vinylmagnesium bromide (11.80 g, 0.09 mol) in dry THF (80 mL), maintained at 55 °C. The mixture was refluxed for 4h, cooled and then hydrolysed with 4N HCl (50mL). The organic layer was extracted with benzene (70 mL). The extract was washed with water and dried with anhydrous Na_2SO_4. The filtrate was added at room temperature to P_2O_5 (10 g) in anhydrous benzene (250 mL) with stirring over a 40 h period. Subsequently the filtrate was evaporated to dryness, giving a crude solid, which was purified by column chromatography over silica gel using hexane as eluent to give **6a** in pure form. Yield 70%; m.p. 65 °C; IR ν_{max} (KBr) 3075 cm^{-1} (=CH_2), 3043 cm^{-1} (=CH), 1625 cm^{-1} (C=C); UV λ_{max} (CH_3CN) 250 (ε 73,000), 330 (ε 2,500), 385 (ε 4,900); ^{1}H NMR ($CDCl_3$) δ 5.66 (1H, dd, J_{trans} = 17.7 Hz, J_{gem} = 2.1 Hz, vinylic), 6.04 (1H, dd, J_{trans} = 11.4 Hz, J_{gem} = 2.1 Hz, vinylic), 7.46-8.40 (10H, m, aromatic and vinylic). Anal. calcd for $C_{16}H_{12}$:C, 94.08; H, 5.92; found: C, 94.31; H, 5.72%.

9-Styrylanthracene (**6b**):[25] A mixture of 9-anthraldehyde (4.12 g, 0.02 mol) and benzyltriphenylphosphonium chloride (8.00 g, 0.02 mol) in dichloromethane (35 mL) was stirred vigorously at room temperature for about 5 min. 50% aqueous solution of NaOH, was then added from a dropping funnel, at the rate of one drop per 7 s. The reaction mixture became a clear brown solution, it was stirred for another 30 min, poured into water and extracted with dichloromethane. The organic layer was separated, washed with water twice and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the pasty residue obtained was recrystallised from 1-propanol, to obtain shining yellow plates of **6b**. Yield 67%; m.p. 131 °C; IR ν_{max} (KBr) 3024 cm^{-1} (=CH), 1621 cm^{-1} (C=C); UV λ_{max} (CH_3CN) 270 (ε 19,800), 300 (ε 7,900), 350 (ε 1,100), 390 (ε 60,000); ^{1}H NMR ($CDCl_3$) δ 6.95 (1H, d, J_{AX} = 16.56 Hz, vinylic), 7.25–8.41 (14H, m, aromatic), 7.92 (1H, d, J_{AX} = 16.56 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 124.87, 125.12, 125.41, 125.98, 126.43, 126.56, 127.96, 128.65, 128.78, 129.71, 131.48, 132.72, 137.26. Anal. calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75; found: C, 94.47; H, 5.42%.

trans-*3-(9-Anthryl)-1-phenylprop-2-en-1-one* (**6c**): [26] A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), acetophenone (2.44 g, 0.02 mol) and potassium hydroxide pellets (1.80 g, 0.03 mol) in methanol (30 mL) was stirred at 60 °C for 48h and later kept in refrigerator for 48h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (1:2) of hexane and dichloromethane to give **6c**. Yield 60%; m.p. 120 °C; IR ν_{max} (KBr) 1653 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 250 (ε 27,400), 330 (ε 6,400), 380 (ε 39,800), 420 (ε 81,700); ^{1}H NMR ($CDCl_3$) δ 7.21 (1H, d, $J_{AX'}$, = 16.2 Hz, vinylic), 7.50–8.50 (14H, m, aromatic), 8.81 (1H, d, J_{AX} = 16.2 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 125.29, 125.41, 126.42, 128.41, 128.73, 128.90, 129.64, 130.17, 131.08, 131.32, 133.05, 137.92, 141.88, 189.68. Anal. calcd for $C_{23}H_{16}O$; C, 89.58; H, 5.23; found: C, 89.20; H, 5.04%.

*Synthesis of 9-alkenyldibenzobarrelenes (**8a–c**); general procedure*

A sample of 9-alkenylanthracenes (**6a–c**, 5 mmol) was dissolved in the minimum quantity of dry xylene and DBA (**7**) (11 mmol) was added. The reaction mixture was refluxed for 12h and progress of the reaction was monitored through TLC. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography. Elution with 1:1 hexane-dichloromethane mixture yielded the corresponding barrelenes.

8a: Yield 93%; m.p. 152 °C; IR ν_{max} (KBr) 1651 (C=O, ketone) cm^{-1}; UV λ_{max} (CH_3CN) 256 (ε 12,080), 300 (ε 2,320); ^{1}H NMR ($CDCl_3$) δ 5.48 (1H, d, J_{trans}=18.2 Hz, vinylic), 5.54 (1H, s, methine), 5.95 (1H, d, J_{cis}=11.5 Hz, vinylic), 6.57–6.65 (1H, m, vinylic), 7.10–7.58 (18H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.25, 59.51, 123.29, 124.03, 124.13, 125.13, 125.65, 128.28, 128.49, 128.64, 128.83, 129.17, 130.13, 133.02, 133.42, 137.01, 137.57, 145.11, 145.33, 151.38, 159.00, 193.94, 195.99; FAB-MS *m/z* 439 (M^++1), 333 (M^+-COPh) and other peaks. Anal. calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06; found: C, 87.79; H, 5.35%.

8b: Yield 91%; m.p. 190 °C; IR ν_{max} (KBr) 1662 (C=O, ketone) cm^{-1}; UV λ_{max} (acetonitrile) 216 (ε 27,040), 256 (ε 15,200), 300 (ε 2,310), 350 nm (ε 470); ^{1}H NMR ($CDCl_3$) δ 5.58 (1H, s, methine), 6.83 (1H, d, J_{AX} =17 Hz, vinylic), 6.91 (1H, d, J_{AX} =17 Hz, vinylic), 7.06–7.59 (23H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.21, 58.92, 121.65, 123.35, 124.02, 125.11, 125.63, 126.38, 128.10, 128.23, 128.41, 128.63, 128.76, 129.15, 129.79, 132.98, 133.31, 136.68, 136.95, 137.56, 138.54, 145.02, 145.72, 151.57, 159.09, 193.92, 196.02. Anal. calcd for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09; found: C, 89.10; H, 5.31%.

8c: Yield 86%; m.p. 120 °C; IR ν_{max} (KBr) 1650, 1665 (C=O, ketone) cm^{-1}; UV λ_{max} (CH_3CN) 254 (ε 12,330), 300 (ε 3,900); ^{1}H NMR ($CDCl_3$) δ 5.58 (1H, s, methine), 7.13–7.77 (24H, m, aromatic and vinylic), 7.89 (1H, d, J_{AX} = 16.5 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 53.21, 58.90, 122.81, 124.20, 125.37, 125.93, 128.31, 128.65, 128.78, 129.12 133.02, 133.15, 133.65, 136.74, 137.26, 139.36, 144.58, 144.74, 151.67, 157.65, 189.62, 193.73, 195.57; FAB-MS *m/z* 543 (M^++1), 437 (M^+-COPh) and other peaks. Anal. calcd for $C_{39}H_{26}O_3$: C, 86.32; H, 4.83; found: C, 86.54; H, 5.11%.

Photochemical reactions of dibenzobarrelenes **8a–c**

A degassed solution of barrelenes (**8a–c**, 0.8 mmol) in benzene (100 mL) was irradiated using RPR 300 nm lamp for 10h. Progress of the reaction was monitored by TLC. Removal of the solvent under reduced pressure gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of dichloromethane and hexane gave unchanged starting materials (21 to 33%). Further elution with a mixture (3:2) of dichloromethane and hexane gave the corresponding dibenzocyclooctatetraene products **11a–c** (58–65%).

11a: Yield 65%; m.p. 108 °C; IR ν_{max} (KBr) 1659 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.96 (1H, d, J_{AX} = 16.9 Hz, vinylic), 5.26 (1H, d, J_{AX} = 10.7 Hz, vinylic), 6.66–6.73 (1H, m, vinylic), 7.12–8.11 (18H, m, aromatic), 7.64 (1H, s, vinylic); ^{13}C NMR ($CDCl_3$) δ 121.21, 126.56, 127.39, 127.44, 127.83, 127.99, 128.24, 128.35, 128.67, 128.88, 129.00, 129.27, 129.70, 129.91, 130.02, 130.62, 130.75, 130.92, 131.26, 132.24, 132.49, 132.75, 133.78, 135.27, 135.69, 136.26, 136.51, 136.77, 137.87, 140.78, 141.03, 141.24, 144.47, 196.12, 197.66; FAB-MS *m/z* 439 (M^++1), 333 (M^+-COPh) and other peaks. Anal. calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06; found: C, 87.42; H, 4.88%.

11b: Yield 62%; m.p. 182 °C; IR ν_{max} (KBr) 1667 (C=O, ketone), 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.21 (1H, d, J_{AX} = 16.0 Hz, vinylic), 7.10–8.12 (19H, m, aromatic and vinylic), 7.67 (1H, s, vinylic) ; FAB-MS *m/z* 453 (M^++1), 347 (M^+-COPh) and other peaks. Anal. calcd for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09; found: C, 89.01; H, 5.35%.

11c: Yield 58%; m.p. 170 °C; IR ν_{max} (KBr) 1664 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) 7.12–7.96 (26H, m, aromatic and vinylic); ^{13}C NMR ($CDCl_3$) δ121.89, 123.64, 124.76, 125.54, 125.87, 126.08, 127.38, 127.68, 127.76, 128.11, 128.25, 128.35, 128.59, 128.80,128.89, 129.13, 129.15, 129.77, 129.83, 130.14, 130.47, 131.13, 131.86, 132.23, 132.39, 133.56, 136.11, 136.35, 136.64, 137.83, 140.64, 142.88, 143.39, 148.07, 195.29, 196.80; FAB-MS *m/z* 543 (M^++1), 437 (M^+-COPh) and other peaks. Anal. calcd for $C_{39}H_{26}O_3$: C, 86.32; H, 4.83; found: C, 86.59; H, 5.01%.

Control experiment using dibenzobarrelene **12**

A degassed solution of barrelene **12** (0.8 mmol) in benzene (100 mL) was irradiated using RPR 300 nm lamp for 30 minutes. Progress of the reaction was monitored by TLC. Removal of the solvent under reduced pressure gave a residual solid, which was recrystallised from a mixture (1:1) of dichloromethane and ethanol to give the corresponding dibenzosemibullvalene **13** (94%). Characterisation data for compounds **12** and **13** are available in the literature.[18]

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