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Phototransformations of bridgehead-substituted dibenzobarrelenes. Steady state and laser flash photolysis studies of 9-benzoyl- and 9-(α-hydroxybenzyl)-substituted dibenzobarrelenes [1]

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Abstract

The photochemistry of 9-benzoyl- and 9-(α-hydroxybenzyl)-substituted dibenzobarrelenes (**1** and **8**) was investigated by steady state photolysis, product analysis and laser flash photolysis. The irradiation of **1** in benzene gave a 91% yield of the dibenzosemibullvalene **6**, and its structure was confirmed by X-ray crystallographic analysis. The 9-(α-hydroxybenzyl)-substituted dibenzobarrelene (**7**) exists in the cyclic carbinol form **8**, as revealed via X-ray structural determination. The irradiation of **8** in benzene gave a 52% yield of 4H-pyranodibenzopentalene **15**. X-Ray single-crystal diffraction studies confirmed the structure of **15**. The 308 nm laser pulse excitation of **1** and **8** in benzene gave rise to transient phenomena which could be attributed to the triplets, characterized by broad absorption spectra and relatively short lifetimes (0.46–0.83 μs). These transients were quenched by oxygen, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO) and ferrocene at rates in the range $(0.23\text{–}4.05)\times10^{9}\ \mathrm{M^{-1}\ s^{-1}}$. The formation of the observed photoproducts from **1** and **8** was rationalized in terms of di-π-methane rearrangements leading to the dibenzosemibullvalenes **6** and **12** and the subsequent transformation of **12** to give **15**.

Keywords: Dibenzobarrelenes; Laser flash photolysis; Phototransformations; Steady state photolysis

1. Introduction

Several aspects of the photorearrangements of dibenzobarrelenes have been investigated in detail [1–3]. In general, dibenzobarrelenes undergo photorearrangement to give predominantly dibenzocyclooctatetraenes through singlet-state-mediated pathways and dibenzosemibullvalenes or products derived from them through triplet-state-mediated pathways. It has been observed that the bridgehead substituents present in the barrelene substrates have a pronounced effect on the observed regioselectivities. Both electronic and steric effects exerted by the substituents affect the regioselectivity. In this study, we have examined the phototransformations of two dibenzobarrelenes, with benzoyl and hydroxybenzyl substituents at the bridgehead (C9) position, to investigate the role of these substituents in the regioselectivities of these barrelene derivatives. In addition, it was of interest to examine the nature of the transients involved in the phototransformations of these barrelene derivatives through nanosecond laser flash photolysis studies.

2. Experimental details

All melting points are uncorrected and were determined on a Büchi-503 melting point apparatus. The IR spectra were recorded on a Perkin–Elmer model 882 IR spectrophotometer. The electronic spectra were recorded on a Shimadzu UV-2100 spectrophotometer. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL EX-90 NMR spectrometer using tetramethylsilane as internal standard. The mass spectra were recorded on a Finnigan MAT model 8430 or a JEOL JMS AX505HA mass spectrometer. All steady state irradiations were carried out in a Srinivasan–Griffin Rayonet photochemical reactor (RPR, 3000 Å light source) or by using Pyrex-filtered light from a Hanovia 450

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W medium pressure mercury vapor lamp. Solvents for photolysis experiments were purified and distilled before use. Aldrich gold-label or Fisher spectral grade solvents were used for laser studies. 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO), from Aldrich, were used as received, whereas ferrocene and β-carotene were recrystallized from ethanol and a mixture of chloroform and ethanol (1:1) respectively before use.

2.1. *Starting materials*

Dibenzoylacetylene (DBA) [4] (melting point (m.p.), 110–111 °C), 9-benzoylanthracene [5] (m.p., 177–178 °C) and 9-hydroxybenzyl-10-methylanthracene [6] (m.p., 155–156 °C) were prepared by reported procedures.

2.2. *Preparation of 1*

The dibenzobarrelene **1** was prepared by stirring a mixture of 9-benzoylanthracene (1.41 g, 5 mmol), DBA (1.17 g, 5 mmol) and anhydrous aluminum chloride (670 mg, 5 mmol) in dry methylene dichloride at room temperature for 30 min and pouring over crushed ice. The mixture was extracted with chloroform and the solvent was removed under reduced pressure to give a solid residue, which was chromatographed over silica gel. Elution with a mixture (1 : 9) of ethyl acetate and petroleum ether gave 1.5 g (58%) of **1** (m.p., 199–200 °C). IR ν_{max} (KBr): 1679 (C=O) cm^{-1}. UV λ_{max} (CH_3CN): 250 nm ($\epsilon = 39\,700$). ^1H NMR ($CDCl_3$) δ: 5.5 (1 H, s, bridgehead proton), 7.0–7.9 (23 H, m, aromatic). ^{13}C NMR ($CDCl_3$) δ: 54.33, 68.32, 123.72, 125.12, 125.57, 125.90, 127.84, 128.20, 128.59, 128.70, 130.05, 132.55, 132.91, 133.12, 136.58, 137.27, 144.07, 152.96, 153.56, 193.83 (C=O), 194.52 (C=O), 196.85 (C=O). Mass spectrum *m/z* (relative intensity): 516 (M^+, 25), 411 (13), 282 (14), 205 (10), 105 (100), 77 (19). Molecular weight calculated for $C_{37}H_{24}O_3$, 516.1725; found, 516.1730 (high-resolution mass spectrometry).

2.3. *Preparation of 8*

The dibenzobarrelene **8** was prepared by refluxing a mixture of 9-hydroxybenzyl-10-methylanthracene (1.49 g, 5 mmol) and DBA (1.17 g, 5 mmol) in toluene for 36 h. The solvent was removed under reduced pressure and the residual solid, after triturating with methanol, was filtered and recrystallized from benzene to give 1.5 g (56%) of **8** (m.p., 218–219 °C). IR ν_{max} (KBr): 3367 (OH), 1647 (C=O) cm^{-1}. UV λ_{max} (CH_3CN): 220 nm ($\epsilon = 40\,000$), 260 nm ($\epsilon = 14\,500$). ^1H NMR ($CDCl_3$) δ: 1.85 (3 H, s, CH_3), 3.15 (1 H, broad s, OH, D_2O-exchangeable), 6.45–8.05 (24 H, m, CH and aromatic). ^{13}C NMR ($CDCl_3$) δ: 13.54, 52.23, 63.03, 77.77, 101.19, 121.37, 122.37, 123.69, 123.99, 124.13, 125.12, 125.33, 126.25, 126.55, 127.54, 127.63, 127.89, 128.19, 128.64, 128.94, 133.14, 136.73, 138.13, 139.83, 144.27, 145.77, 146.0, 148.24, 148.33, 159.64, 195.38 (C=O). Mass spectrum *m/z* (relative intensity): 532 (M^+, 17), 514 (26), 427 (13), 409 (21), 305 (27), 105 (100), 72 (13). Molecular weight calculated for $C_{38}H_{28}O_3$, 532.2038; found, 532.2064 (high-resolution mass spectrometry).

2.4. *Photolysis of 1*

The irradiation of a benzene solution of **1** (258 mg, 0.5 mmol in 250 ml) for 30 min (Hanovia 450 W medium pressure lamp source) and removal of the solvent under reduced pressure gave a residual solid, which was recrystallized from carbon tetrachloride to give 235 mg (91%) of **6** (m.p., 202–203 °C). IR ν_{max} (KBr): 1669 (C=O) cm^{-1}. UV λ_{max} (CH_3CN): 252 nm ($\epsilon = 54\,600$). ^1H NMR ($CDCl_3$) δ: 5.05 (1 H, s, 4b-H), 6.80–7.95 (23 H, m, aromatic). ^{13}C NMR ($CDCl_3$) δ: 29.65, 59.30, 67.21, 77.80, 121.75, 127.15, 127.36, 127.95, 128.37, 128.97, 130.04, 132.40, 134.99, 136.34, 137.92, 150.63, 159.16, 194.16 (C=O), 194.81 (C=O). Molecular weight calculated for $C_{37}H_{24}O_3$, 516.1725; found, 516.1725 (high-resolution mass spectrometry).

2.5. *Photolysis of 8*

The irradiation of **8** (200 mg, 0.38 mmol in 200 ml of benzene) for 1 h (RPR 3000 Å light source) and removal of the solvent under reduced pressure gave a solid, which was recrystallized from benzene to give 100 mg (52%) of **15** (m.p., 268–269 °C). IR ν_{max} (KBr): 1670 (C=O), 1242, 1070 and 764 cm^{-1}. UV λ_{max} (CH_3CN): 249 nm ($\epsilon = 9130$), 311 nm ($\epsilon = 6940$). ^1H NMR ($CDCl_3$) δ: 1.80 (3 H, s, CH_3), 6.90–8.00 (23 H, m, aromatic). ^{13}C NMR ($CDCl_3$) δ: 25.74, 59.64, 120.95, 121.16, 123.99, 127.87, 127.99, 128.47, 128.67, 129.00, 129.45, 129.75, 132.08, 133.36, 136.91, 137.71, 148.78, 157.58, 200.67 (C=O). Molecular weight calculated for $C_{38}H_{26}O_2$, 514.1939; found, 514.1937 (high-resolution mass spectrometry).

Further elution of the silica gel column with the same solvent gave 80 mg (40%) of the unchanged dibenzobarrelene **8** (m.p., 218–219 °C).

2.6. *X-Ray structural determination of 6, 8 and 15*

Colorless crystals of **6**, **8** and **15** with appropriate dimensions were subjected to X-ray crystallographic analysis. Data were collected using Mo radiation at room temperature with a Siemans P_4 diffractometer, and data reduction, structure solution and refinement were carried out using the SHELX-TL package for structure determination [7]. Full-matrix least-squares refinement was carried out on F^2 and all non-hydrogen atoms were refined anisotropically to convergence.

2.7. *Laser flash photolysis*

Pulse excitation was carried out at 308 nm employing a Lambda-Physik EMG 101 MCS excimer laser (50 mJ, 10 ns, XeCl) and at 337.1 nm (8 ns, 2–3 mJ) using a Molectron UV-400 nitrogen laser source. The output from the excimer laser was suitably attenuated to approximately 20 mJ per pulse or less and defocused to minimize multiphoton processes. The transient phenomena were studied using a kinetic spectrometer described elsewhere [8,9]. Unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon. In experiments in which a large number of laser shots were necessary, e.g. for wavelength-by-wavelength measurements to give transient absorption spectra, a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through a cell.

3. Results

3.1. *Preparative photochemistry and product identification*

The dibenzobarrelene **1** was prepared (58%) by the treatment of 9-benzoylanthracene with DBA in the presence of anhydrous aluminum chloride, whereas **8** was obtained (56%) by refluxing an equimolar mixture of 9-(α-hydroxybenzyl)-10-methylanthracene and DBA in dry toluene. Both **1** and **8** were characterized on the basis of analytical results and spectral data. In addition, the structure of **8** was confirmed by X-ray crystallographic analysis.

The irradiation of **1** in benzene gave a 91% yield of the dibenzofuranopentalene **6**. The structure of **6** was established on the basis of analytical results and spectral data. The IR spectrum of **6**, for example, showed a C=O absorption at 1669 cm^{-1}. Its ^1H NMR spectrum showed a singlet at $\delta = 5.10$ due to the 4b proton and a complex multiplet centered around $\delta = 7.40$ due to the aromatic protons. The ^{13}C NMR spectrum of **6** showed signals due to four sp^3 carbons and two signals at $\delta = 194.16$ and 194.81 characteristic of ketone carbonyl carbons. The structure of **6** was confirmed by X-ray crystallographic analysis.

The irradiation of **8** in benzene (1 h) gave a 52% yield of the 4H-pyranodibenzopentalene **15**, together with 40% recovery of the unchanged starting material. The IR spectrum of **15** did not show any OH absorption band, but a carbonyl band at 1670 cm^{-1}. The ^1H NMR spectrum of **15** showed a singlet at $\delta = 1.80$ due to the methyl protons and a multiplet centered around $\delta = 7.45$ due to the aromatic protons. Confirmation of the structure of **15** was derived by single-crystal X-ray diffraction studies.

3.2. *X-Ray crystallographic analysis of 6, 8 and 15 [10]*

Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters of $a = 10.969$ Å, $b = 27.50$ Å and $c = 9.597$ Å. The angle β has been found to be 114.64°. Compound **8** crystallizes in the triclinic space group $P\bar{1}$ with the following parameters: $a = 10.261$ Å, $b = 10.740$ Å, $c = 13.870$ Å, $\alpha = 77.16°$, $\beta = 72.62°$, $\gamma = 75.56°$ and $V = 1394.5$ $Å^3$. Compound **15** crystallizes in the monoclinic, non-chiral space group $P2_1/c$ with the unit cell dimensions $a = 11.193$ Å, $b = 14.313$ Å and $c = 17.366$ Å. The angle β has been found to be 105.26°. The projection view diagrams of **6**, **8** and **15** are shown in Figs. 1–3. In compound **6**, the cyclopropane ring is intact and has three benzoyl substituents. These groups are spatially spread out to cause the minimum

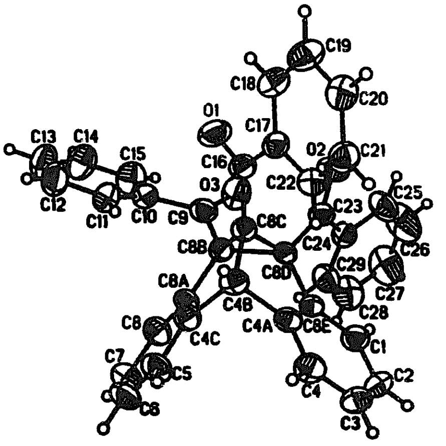


Fig. 1. Projection view of **6** with 50% probability ellipsoids.

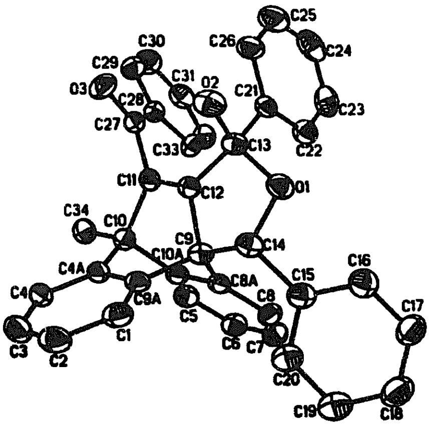


Fig. 2. Projection view of **8** with 30% probability ellipsoids.

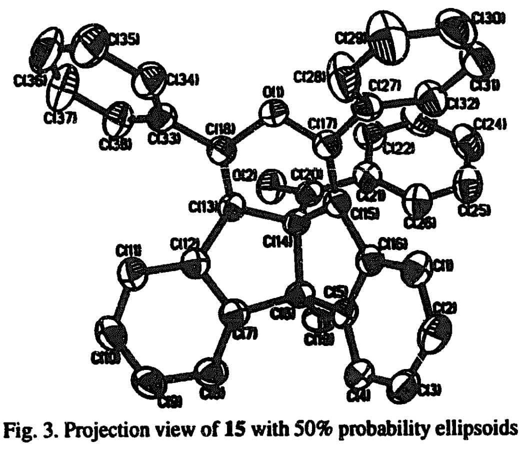


Fig. 3. Projection view of **15** with 50% probability ellipsoids.

steric strain. The formation of the five-membered ring, involving the α-hydroxy group of the bridgehead substituent at C9 and the benzoyl group attached to C12, distorts the bond angles and distances in **8** to some extent. Thus, whereas the C27–C11–C12 angle is 124.2°, the corresponding C11–C12–C13 angle is 133.1°. Compound **15** incorporates a pentacyclic 6,5,6,5,6 fused ring core which has the shape of a shallow bowl. The angles between the two five-membered rings at C13–C14–C15 and C5–C6–C7 are 105.9° and 114.6° respectively and are unequal. Both the methyl group at the C6 position and the benzoyl group at the C14 position are on the same side as would be expected for substituents at the fused ring junctions on the dibenzopentalene skeleton.

3.3. *Laser flash photolysis studies*

Laser flash photolysis (308 nm) of a benzene solution of **1** results in the formation of a transient species, characterized by a broad absorption spectrum at 300–700 nm, with two maxima at 350 nm and 620 nm. The transient spectrum of **1** is shown in Fig. 4. Both of these absorption maxima pertain to one single transient as shown by the nearly identical lifetimes of 0.48 μs and 0.46 μs when monitored at 350 and 620 nm respectively. In addition, the phototransient from **1** is efficiently quenched by oxygen with nearly identical rate constants of $k_q = 0.66 \times 10^9$ M^{-1} s^{-1} and $k_q = 0.61 \times 10^9$ M^{-1} s^{-1} when monitored at 350 and 620 nm respectively. We assign this transient to the triplet of **1** on the basis of its quenching behavior with oxygen and other triplet quenchers.

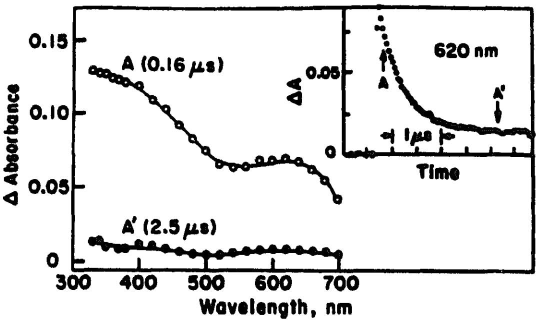


Fig. 4. Transient absorption spectra at the indicated times following 308 nm laser excitation of **1** (A, A') in deaerated benzene. Inset: kinetic trace of the transient absorption decay at 620 nm as observed for **1**.

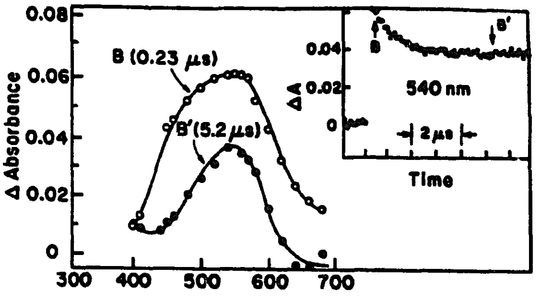


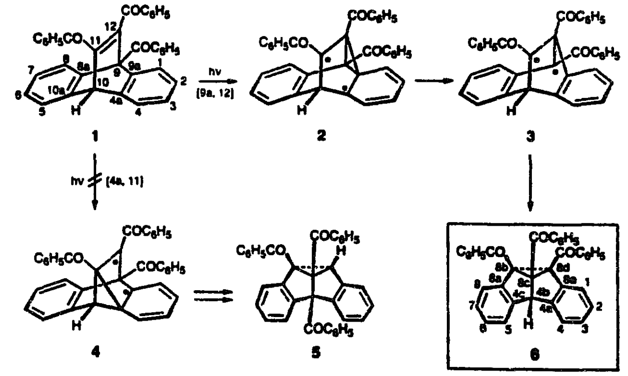
Fig. 5. Transient absorption spectra at the indicated times following 308 nm laser excitation of **8** (B, B') in deaerated benzene. Inset: kinetic trace of the transient absorption decay at 540 nm as observed for **8**.

Thus it is quenched efficiently by TEMPO ($k_q = 0.17 \times 10^9$ M^{-1} s^{-1}), HTEMPO ($k_q = 0.24 \times 10^9$ M^{-1} s^{-1}), ferrocene ($k_q = 3.87 \times 10^9$ M^{-1} s^{-1}) and β-carotene ($k_q = 3.27 \times 10^9$ M^{-1} s^{-1}). With β-carotene as quencher, the growth of an intense transient absorption due to the β-carotene triplet is observed at 510–550 nm on the same timescale as that of the decay of the triplet of **1**. The triplet yield $\phi^T = 0.65$ and $\epsilon^T_{max} = 4.33 \times 10^3$ M^{-1} cm^{-1} were obtained by comparative techniques, using benzophenone triplet ($\phi^T = 1$, $\epsilon^T_{max} = 7.6 \times 10^3$ M^{-1} cm^{-1}) formation in benzene for actinometry and β-carotene as a triplet counter as reported previously [1,11].

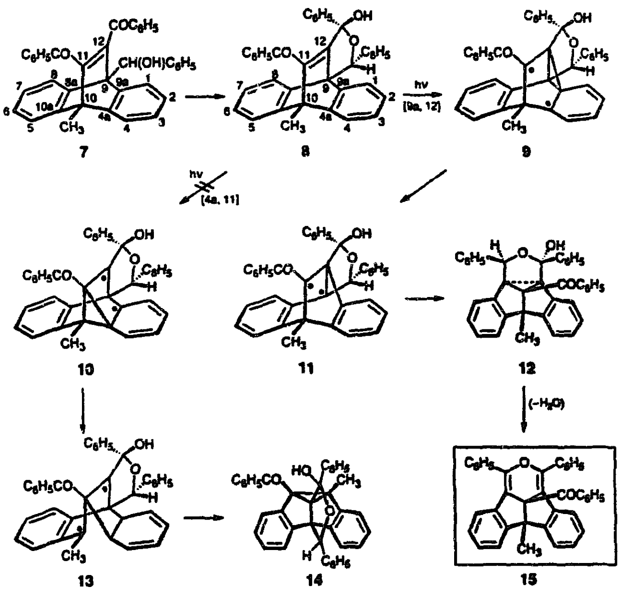
Laser excitation (308 nm, 10 ns) of **8** in benzene gives a transient with an absorption maximum at 540 nm, formed within nanoseconds of the laser pulse. The transient spectrum of **8** is shown in Fig. 5. The transient decays by first-order kinetics with a lifetime of 0.83 μs. A residual absorption is observed following the decay of the initial transient (see part B' in Fig. 5), which does not show any decay over our longest timescale (approximately 100 μs). The initially formed transient is efficiently quenched by oxygen ($k_q = 0.23 \times 10^9$ M^{-1} s^{-1}), TEMPO ($k_q = 0.54 \times 10^9$ M^{-1} s^{-1}), HTEMPO ($k_q = 0.8 \times 10^9$ M^{-1} s^{-1}) and ferrocene ($k_q = 4.05 \times 10^9$ M^{-1} s^{-1}) and is assigned, on the basis of this quenching behavior, to the triplet of **8**.

4. Discussion

The di-π-methane rearrangement of bridgehead-substituted dibenzobarrelenes, such as **1** and **8**, can, in principle, proceed through multichannel pathways, leading to regioisomeric dibenzosemibullvalenes. Thus an initial [9a,12] benzo–vinyl bridging in **1** would give rise to the diradical intermediates **2**, which could undergo further reorganization to the diradical intermediates **3** and would ultimately lead to the dibenzosemibullvalenes **6** (Scheme 1). In contrast, if [4a,11] bridging is operative, we would obtain the regioisomeric dibenzosemibullvalene **5**. It is interesting to note that the dibenzosemibullvalene **6**, containing three benzoyl groups attached to the cyclopropane ring, is relatively stable and can be isolated as such. In contrast, the dibenzosemi-



Scheme 1.



Scheme 2.

bullvalenes, derived from 9-aryl-substituted dibenzobarrelenes, are unstable at room temperature and undergo ring enlargement reactions, leading to the corresponding dibenzofuranopentalenes [2]. It is probable that the presence of three electron-withdrawing benzoyl groups attached to the cyclopropane ring in **6** will prevent ionic opening of this ring system.

Similarly, an initial [9a,12] benzo–vinyl bridging in **8** would give the diradical intermediate **9**, which could then lead to the dibenzosemibullvalene derivative **12** via a second diradical intermediate. Elimination of water from **12**, under the reaction conditions, would lead to the dibenzopyranopentalene **15**, as shown in Scheme 2.

The fact that both **6** and **15** are the only observed products from **1** and **8** respectively suggests that the phototransformations of **1** and **8** proceed in a regioselective manner. In both of these cases, the preferred pathway appears to involve an initial [9a,12] bridging and not [4a,11] bridging. A plausible explanation for this preference could be that both **1** and **8**, containing bulky substituents at the C9 position, will experience appreciable steric strain due to the interaction between the C9 substituent and the C1 and C8 hydrogen atoms. The benzo–vinyl bridging involving a [9a,12] interaction eventually leads to release of this steric interaction and hence favors the observed pathways in both **1** and **8**.

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