

# Steady state photolysis of bridgehead disubstituted dibenzobarrelenes and thermal isomerization of their photoproducts<sup>☆</sup>

Meledathu C. Sajimon<sup>a</sup>, Danaboyina Ramaiah<sup>a,\*</sup>, Mohammad Muneer<sup>a,d</sup>,  
Nigam P. Rath<sup>b</sup>, Manapurathu V. George<sup>a,c,1</sup>

<sup>a</sup> Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

<sup>b</sup> Department of Chemistry, University of Missouri-St. Louis, Missouri, MO 63121, USA

<sup>c</sup> Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India

<sup>d</sup> Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

Received 29 February 2000; received in revised form 27 June 2000; accepted 11 July 2000

## Abstract

The photorearrangements of a few bridgehead disubstituted dibenzobarrelenes **5a–c** and thermal transformations of their primary photoproducts **8a–c** are described. Irradiation of 9-acetyl-10-methyl-substituted dibenzobarrelene **5a** in benzene gave a mixture of the regioselective *8b*-acetyl substituted dibenzosemibullvalene **8a** (74%), involving a di- $\pi$ -methane rearrangement and a novel polycyclic ketone **11** (7%), through  $\delta$ -hydrogen abstraction. Irradiation of the disubstituted dibenzobarrelenes **5b** and **5c**, under identical conditions, gave the corresponding dibenzosemibullvalene derivatives **8b** (85%) and **8c** (81%), respectively. Interestingly, compound **8a** underwent a facile reaction with methanol to give the acetal derivative **15**. Thermolysis of the semibullvalene derivative **8a** at 180–200°C for 2 h gave a dibenzopentalenofuran **12a**, in 92% yield. Similarly, thermal transformations of **8b** and **8c**, under analogous conditions, gave the corresponding pentalenofurans **12b** and **12c**, respectively, in nearly quantitative yields. The kinetics of the thermal isomerization reactions were studied and the activation energies of **8a–c** to **12a–c** have been found to be 21.04, 23.42 and 24.74 kcal mol<sup>-1</sup>, respectively. The structures of **5a**, **8c**, **11** and **15** were established unambiguously through X-ray crystallographic analysis. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Dibenzobarrelenes; Dibenzopentalenofurans; Dibenzosemibullvalenes di- $\pi$ -methane rearrangement;  $\delta$ -Hydrogen abstraction

## 1. Introduction

The di- $\pi$ -methane rearrangement has attracted much attention of organic chemists because of its importance in organic synthesis as well as its interesting mechanistic aspects [1–5]. The generality of this reaction for acyclic, monocyclic and condensed polycyclic systems can be used as a potential synthetic method for a variety of polycyclic ring compounds, which are of pharmaceutical interest [6]. Several aspects of the phototransformations of dibenzobarrelenes are reported in the literature [1–5,7–13]. In general, they undergo photorearrangement, leading primarily to dibenzocyclooctatetraenes and dibenzosemibullvalenes. It has been shown that the dibenzocyclooctatetraenes are formed under direct irradiation, through a singlet state mediated pathway, whereas

the dibenzosemibullvalenes are formed through a triplet state mediated di- $\pi$ -methane rearrangement [7–13].

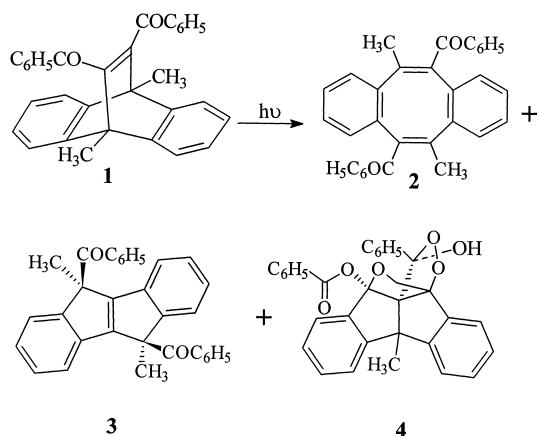
In earlier studies, we had reported that the bridgehead substituted dibenzobarrelenes, containing dibenzoylalkene moieties undergo phototransformations, channeled by the dibenzobarrelene chromophore [14–17]. Both electronic and steric effects of the bridgehead substituents, even though not fully understood, play a major role in the observed regioselectivity of these rearrangements. Further, it has been observed that the primary photoproducts, namely dibenzosemibullvalenes undergo secondary transformations depending on the substituents present in them and also on the reaction conditions. Thus, for example, irradiation of a symmetrical disubstituted dibenzobarrelene such as **1** gave a mixture of the dibenzocyclooctatetraene **2** and the dibenzopentalene derivative **3**, in addition to an oxygenated hexacyclic peroxy carbinol **4**, formed through the oxygen trapping of diradical intermediates (Scheme 1) [17]. In contrast, the irradiation of 9,10-dimethoxy-substituted dibenzobarrelene, in acetone gave exclusively a pentalenofuran derivative [16]. However, when the irradiation was carried out in a mixture of benzene

<sup>☆</sup> Contribution No. RRLT-PRU-111 from the Regional Research Laboratory (CSIR), Trivandrum, India.

\* Corresponding author. Tel.: +91-471-491712; fax: +91-471-490186.

E-mail address: rama@csrrltd.ren.nic.in (D. Ramaiah).

<sup>1</sup> Co-corresponding author.



Scheme 1.

and aqueous methanol, a mixture of pentacyclic methanol adduct and a dibenzopentalenone derivative have been isolated. These studies show that the photolysis of appropriately substituted dibenzobarrelenes could be a potential synthetic route to the synthesis of several polycyclic ring systems.

The objective of the present investigation has been to examine the photochemical transformations of a few bridgehead disubstituted dibenzobarrelenes with a view to study the nature of the products formed in these cases and also the role of the substituents on the regioselectivity in these rearrangements. Yet another objective has been to study the thermal isomerization of the dibenzosemibullvalene derivatives, formed as primary photoproducts in these reactions and also the kinetics of these transformations. The dibenzobarrelenes that we have examined include **5a** (9-acetyl-11,12-dibenzoyl-9,10-dihydro-10-methyl-9,10-ethenoanthracene) and related compounds, **5b** and **5c**. The photoproducts that we have subjected to thermal isomerization include **8a** (8b-acetyl-8c,8d-dibenzoyl-4b-methyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclo-propa[c,d]pentalene) and related compounds, **8b** and **8c**.

## 2. Experimental details

The equipment and procedures for melting point determination and spectral recordings are described in earlier publications [16,18,19]. All steady state irradiation experiments were carried out in a Srinivasan-Griffin-Rayonet Photochemical Reactor (RPR 300 nm) or by using Pyrex filtered light from a Hanovia 450 W medium pressure mercury lamp. Solvents for photolysis experiments were purified and distilled before use. Petroleum ether used was the fraction with a bp 60–80°C.

## 3. Starting materials

Dibenzoylacetylene (DBA) [20,21] (mp, 110–111°C), 9-acetyl-10-methylan-thracene (prepared from 9-methyl-

anthracene by Friedel-Crafts acylation [22]) (mp, 135–136°C), 9-benzoyl-10-methylan-thracene [23] (mp, 175–176°C), and 9-benzoyl-10-methoxyanthracene [24] (mp, 174–175°C), were prepared by reported procedures.

### 3.1. Preparation of **5a**, **5b** and **5c**

#### 3.1.1. Compound **5a**

An equimolar mixture of 9-acetyl-10-methylan-thracene (2.34 g, 10 mmol) and DBA (2.34 g, 10 mmol) under neat heating at 140–170°C for 5 h gave a product mixture, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and hexane gave 820 mg (35%) of the unchanged anthracene derivative (mp, 135–136°C) (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 2.16 g (47%) of **5a** (mp, 226–227°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr):  $\nu_{\max}$  3054, 1731, 1667  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  256 nm ( $\epsilon$  33,900). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.06 (3H, s, methyl), 2.47 (3H, s, acetyl), 6.87–7.86 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.90, 31.99, 51.56, 68.03, 121.26, 125.42, 125.53, 128.10, 128.48, 133.31, 136.90, 144.28, 146.80, 157.75, 194.42, 195.01, 204.17. Mol wt. calcd. for C<sub>33</sub>H<sub>24</sub>O<sub>3</sub> (M + H)<sup>+</sup> 469.1804, found 469.1813 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>33</sub>H<sub>24</sub>O<sub>3</sub>: C, 84.61; H, 5.13. Found: C, 84.32; H, 5.13.

#### 3.1.2. Compound **5b**

An equimolar mixture of 9-benzoyl-10-methylan-thracene (2.93 g, 10 mmol) and DBA (2.34 g, 10 mmol) under neat heating at 140–170°C for 5 h gave a solid residue, which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of ethyl acetate and hexane gave 900 mg (30%) of the unchanged anthracene derivative (mp, 175–176°C) (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 1.84 g (35%) of **5b** (mp, 216–217°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr):  $\nu_{\max}$  3033, 1658  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  252 nm ( $\epsilon$  32,700). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.07 (3H, s, methyl), 6.91–7.72 (23H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.05, 51.75, 66.14, 121.18, 125.15, 125.23, 128.28, 128.46, 132.80, 137.00, 145.63, 146.30, 150.90, 156.62, 193.70, 195.44, 197.72. Mol wt. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>3</sub> (M+H)<sup>+</sup> 531.1960, found 531.1984 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>3</sub>: C, 86.04; H, 4.90. Found: C, 86.22; H, 5.19.

#### 3.1.3. Compound **5c**

To a mixture of 9-benzoyl-10-methoxyanthracene (1.50 g, 5 mmol) and aluminum chloride (680 mg, 5 mmol) in dichloromethane was added DBA (1.17 g, 5 mmol) in small amounts at 0°C. The reaction mixture was stirred for 1.5 h and poured over crushed ice, acidified with hydrochloric acid (6.5N, 500 ml) and extracted with dichloromethane.

Removal of the solvent gave a solid residue, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and hexane gave 600 mg (40%) of the unchanged anthracene derivative (mp, 174–175°C) (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 534 mg (20%) of **5c** (mp, 246–247°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr):  $\nu_{\max}$  3050, 1666  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  254 nm ( $\epsilon$  22,000). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.86 (3H, s, methoxy), 7.07–7.73 (23H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  57.62, 67.12, 89.50, 121.65, 125.33, 127.92, 128.24, 129.16, 132.80, 137.14, 144.77, 150.62, 154.89, 194.04, 194.30, 196.67. Mol wt. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>4</sub> (M + H)<sup>+</sup> 547.1909, found 547.1909 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>4</sub>: C, 83.52; H, 4.76. Found: C, 83.26; H, 4.88.

### 3.2. Photolysis of **5a**

A solution of **5a** (468 mg, 1 mmol) in benzene (300 ml) was irradiated (Hanovia 450 W) for 45 min. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel, using a chromatotron. Elution with a mixture (1:4) of ethyl acetate and petroleum ether gave 33 mg (7%) of **11** (mp, 231–232°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr):  $\nu_{\max}$  2931, 1737  $\text{cm}^{-1}$ ; UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  293 nm ( $\epsilon$  28,980). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.99 (3H, s, methyl), 6.37 (1H, s, vinylic), 6.78–7.42 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.43, 53.00, 62.44, 120.89, 125.77, 127.33, 128.02, 128.17, 133.29, 137.54, 146.73, 151.53, 164.30, 195.44, 199.41. Mol wt. calcd. for C<sub>33</sub>H<sub>22</sub>O<sub>2</sub> (M + H)<sup>+</sup> 451.1698, found 451.1682 (high-resolution mass spectrometry).

Further elution gave 346 mg (74%) of **8a** (mp, 180–181°C), after recrystallization from a mixture (1:1) of dichloromethane and hexane: IR (KBr):  $\nu_{\max}$  3068, 1721, 1667  $\text{cm}^{-1}$ ; UV (CH<sub>3</sub>CN):  $\lambda_{\max}$  251 nm ( $\epsilon$  32,000). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.67 (3H, s), 2.58 (3H, s, methyl), 6.77–8.02 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.39, 31.12, 62.58, 64.88, 67.04, 80.87, 120.03, 128.15, 128.53, 129.28, 129.77, 138.11, 138.55, 153.39, 154.93, 193.37, 193.86, 202.90. Mol wt. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>4</sub> (M + H)<sup>+</sup> 469.1804, found 469.1793 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>33</sub>H<sub>24</sub>O<sub>3</sub>: C, 84.61; H, 5.13. Found: C, 84.60; H, 4.82.

### 3.3. Photolysis of **5b**

A solution of **5b** (530 mg, 1 mmol) in benzene (100 ml) was irradiated (RPR, 300 nm) for 35 min. The solvent was removed under vacuum and the residual solid thus obtained was triturated with methanol to give 450 mg (85%) of **8b**

(mp, 192–193°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr):  $\nu_{\max}$  3021, 1669  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  255 nm ( $\epsilon$  24,100). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.80 (3H, s), 6.80–8.10 (23H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.46, 62.62, 65.84, 81.41, 119.99, 125.15, 126.94, 127.18, 128.07, 129.51, 132.25, 138.22, 153.58, 193.68, 194.68. Mol wt. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>3</sub> 531.1960, found 531.1974 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>3</sub>: C, 86.04; H, 4.90. Found: C, 86.13; H, 5.08.

### 3.4. Photolysis of **5c**

A solution of **5c** (220 mg, 0.5 mmol) in benzene (200 ml) was irradiated (RPR, 300 nm) for 50 min. Removal of the solvent under vacuum gave a residual solid, which was triturated with methanol to give 178 mg (81%) of **8c** (mp, 212–213°C), after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR (KBr)  $\nu_{\max}$  3046, 1681  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>CN):  $\lambda_{\max}$  273 nm ( $\epsilon$  24,800). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.36 (3H, s, methoxy), 6.81–7.83 (23H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  54.33, 66.05, 80.54, 98.93, 120.84, 127.78, 128.08, 128.35, 129.98, 137.98, 149.30, 191.96, 193.89. Mol wt. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>4</sub> (M + H)<sup>+</sup> 547.1909, found 547.1935 (high-resolution mass spectrometry).

Anal. calcd. for C<sub>38</sub>H<sub>26</sub>O<sub>4</sub>: C, 83.52; H, 4.76. Found: C, 83.34; H, 4.89.

### 3.5. <sup>1</sup>H NMR monitoring of the photoreactions of **5a–c**

Solutions of **5a–c** in CDCl<sub>3</sub> (10 mg in 0.5 ml) in a NMR tube, in each case, were irradiated with RPR 300 nm light source for 30 min and recorded their <sup>1</sup>H NMR spectra. The <sup>1</sup>H NMR spectrum of the photolysis mixture, in each case, confirmed the ratios of photoproducts as reported in the steady state photolysis and product analysis and ruled out the formation of any other detectable products in these phototransformations.

### 3.6. Reaction of semibullvalene derivative **8a** with methanol

A solution of **8a** (250 mg, 0.5 mmol) in methanol was refluxed for 2 h and upon removal of the solvent gave a solid residue, which was recrystallized from a mixture (1:4) of chloroform and methanol to give 215 mg (87%) of **15** (mp, 274–275°C). IR (KBr):  $\nu_{\max}$  3063, 1666  $\text{cm}^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  270 nm ( $\epsilon$  32,000). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.38 (3H, s, methyl), 2.16 (3H, s, methyl), 3.21 (3H, s, methoxy), 3.65 (3H, s, methoxy), 6.78–8.26 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.63, 18.51, 49.53, 50.18, 61.70, 65.59, 74.91, 96.13, 107.23, 107.77, 120.45, 127.40, 127.55, 127.65, 128.43, 134.82, 138.35, 150.39, 150, 73,

192.65. Mol wt. calcd. for  $C_{35}H_{30}O_4$  514.2144, found 514.2168 (high-resolution mass spectrometry).

Anal. calcd. for  $C_{35}H_{30}O_4$ : C, 81.69; H, 5.87. Found: C, 81.99; H, 5.56.

### 3.7. Thermal isomerization of **8a–c** and kinetic measurements

The thermal isomerization of **8a–c** was achieved under neat heating at 180–200°C for 2 h. The residual solid thus obtained was recrystallized from a mixture (4:1) of dichloromethane and methanol to give the corresponding pentalenofurans **12a–c**.

**12a** (92%) (mp, 192–193°C). IR (KBr):  $\nu_{\max}$  3058, 1724, 1661  $cm^{-1}$ . UV  $\lambda_{\max}$  (CH<sub>3</sub>OH): 324 nm ( $\epsilon$  34,500). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.65 (3H, s, methyl), 2.43 (3H, s, acetyl), 7.03–7.55 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.50, 28.96, 60.07, 89.24, 103.13, 120.62, 120.94, 122.86, 123.86, 124.54, 128.01, 128.17, 128.32, 128.40, 130.15, 130.29, 130.62, 131.66, 135.16, 139.52, 140.76, 148.36, 152.35, 153.63, 200.29, 205.36. Mol wt. calcd. for  $C_{33}H_{24}O_3$  (M + H)<sup>+</sup> 469.1804, found 469.1796 (high-resolution mass spectrometry).

**12b** (95%) (mp, 198–199°C). IR (KBr):  $\nu_{\max}$  3067, 1665  $cm^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  321 nm ( $\epsilon$  33,500). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.89 (3H, s, methyl), 7.06–8.26 (18H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.54, 60.42, 89.31, 103.64, 121.18, 121.64, 122.70, 124.41, 124.59, 127.84, 127.90, 128.08, 128.14, 128.31, 130.15, 130.38, 131.23, 132.72, 134.34, 136.84, 139.87, 141.32, 148.27, 151.38, 154.33, 197.50, 199.41. Mol wt. calcd. for  $C_{38}H_{26}O_3$  (M<sup>•+</sup>) 530.1882, found 530.1888 (high-resolution mass spectrometry).

**12c** (87%) (mp, 202–203°C). IR (KBr):  $\nu_{\max}$  3029, 1627  $cm^{-1}$ . UV (CH<sub>3</sub>OH):  $\lambda_{\max}$  321 nm ( $\epsilon$  32,400). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.26 (3H, s, methoxy), 7.11–8.17 (23H, m, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  54.67, 69.11, 98.44, 101.42, 119.09, 123.71, 127.24, 127.59, 128.29, 130.32, 134.71, 140.67, 145.09, 150.79, 197.77, 200.21. Mol wt. calcd. for  $C_{38}H_{26}O_4$  (M + H)<sup>+</sup> 547.1909, found 547.1912 (high-resolution mass spectrometry).

The kinetics of thermal isomerization of **8a–c** to **12a–c** was studied by UV spectroscopy, using *n*-decane as solvent and the studies were carried out as reported earlier [25]. A degassed solution of **8a** in *n*-decane ( $6.25 \times 10^{-5}$  M) was heated with stirring at 110°C and aliquots were removed after each 5 min time intervals to record the UV spectrum. The formation of the product was observed by monitoring the absorption change at 324 nm, which is characteristic of the dihydropentalenofuran derivative **12a**. Similarly, the experiment was repeated at 115 and 120°C, to measure the corresponding rate constants. The thermal isomerization of **8b** ( $8 \times 10^{-5}$  M) was followed by monitoring the absorption change at 321 nm (characteristic absorption of **12b**) and repeated the experiment at three different temperatures, namely, 140, 145 and 155°C. The thermal isomerization of

**8c** ( $8 \times 10^{-5}$  M) in *n*-decane, was similarly carried out at three different temperatures (140, 145 and 150°C) and the progress of the reaction was monitored at 321 nm (characteristic absorption of **12c**).

### 3.8. X-ray structure determination of **5a**, **8c**, **11** and **15**

Good quality crystals of **5a**, **8c**, **11** and **15** were mounted on glass fibers in random orientations and subjected to X-ray crystallographic analysis, employing Siemens R3 automated four circle diffractometer. Data reduction and structure solution were achieved by SHELXTL-PLUS (VMS) structure solution package [25]. Crystallographic data of **5a**, **8c**, **11** and **15** are summarized in Table 1.

## 4. Results

### 4.1. Steady state photolysis and product identification

The starting dibenzobarrelenes containing 1,2-dibenzoyl-alkene moieties were conveniently prepared through the reaction of the appropriate anthracenes with dibenzoylacetylene (DBA) under neat heating or in the presence of a Lewis acid catalyst such as aluminum chloride. All dibenzobarrelenes have been fully characterized by analytical results and spectral data. Structure of the dibenzobarrelene **5a** (Fig. 1) was confirmed through X-ray crystallographic analysis [25] (Table 2).

Photolysis of **5a** in benzene gave a mixture of products consisting of the regioselective dibenzosemibullvalene **8a** and polycyclic ketone **11** in 74 and 7% yields, respectively (Scheme 2). In contrast, the irradiation of **5b** and **5c**, under similar conditions, gave **8b** (85%) and **8c** (81%), respectively, as the exclusive products. The <sup>1</sup>H NMR spectrum

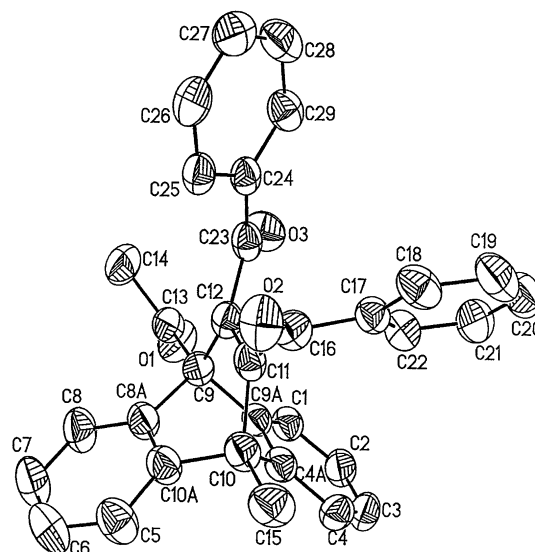


Fig. 1. Projection view of **5a** with 50% probability ellipsoids.

Table 1  
Crystallographic data for compounds **5a**, **8c**, **11** and **15**

| Parameters   | <b>5a</b>  | <b>8c</b>  | <b>11</b>  | <b>15</b>  |
|--|--|--|--|--|
| Empirical formula  | C <sub>33</sub> H <sub>24</sub> O <sub>3</sub>                 | C <sub>38</sub> H <sub>26</sub> O <sub>4</sub>                   | C <sub>33</sub> H <sub>22</sub> O <sub>2</sub>                 | C <sub>35</sub> H <sub>30</sub> O <sub>4</sub>                   |
| <i>M<sub>w</sub></i>   | 468.52   | 546.59   | 450.51   | 514.59   |
| <i>T</i> (K)   | 223 (2)  | 298 (2)  | 223 (2)  | 298 (2)  |
| $\lambda$ (Å)  | 0.71073  | 0.71073  | 0.71073  | 0.71073  |
| Crystal system   | Triclinic  | Orthorhombic   | Triclinic  | Orthorhombic   |
| Space group  | P1   | P2(1)2(1)2(1)  | P1   | P2(1)2(1)2(1)  |
| <i>a</i> (Å)   | 9.6635 (1)   | 10.5323 (1)  | 9.40880 (10)   | 11.3948 (4)  |
| <i>b</i> (Å)   | 9.9006 (1)   | 15.9480 (2)  | 10.5062 (2)  | 12.2208 (4)  |
| <i>c</i> (Å)   | 13.2321 (2)  | 17.2175 (2)  | 12.9670 (10)   | 18.8913 (7)  |
| <i>V</i> (Å <sup>3</sup> )                                   | 1215.82 (3)  | 2908.48 (6)  | 1171.15 (3)  | 2630.68 (16)   |
| <i>Z</i> , $\rho_{\text{calcd}}$ (Mg m <sup>-3</sup> )       | 1.280  | 4  | 1.278  | 4  |
| $\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )                   | 0.081  | 0.080  | 0.078  | 1.299  |
| <i>F</i> (000)   | 492  | 1144   | 472  | 1088   |
| Crystal size (mm)  | 0.42 × 0.40 × 0.34   | 0.40 × 0.20 × 0.20   | 0.42 × 0.38 × 0.33   | 0.38 × 0.24 × 0.08   |
| $\theta$ range for data collection (°)                       | 1.60–26.00   | 1.74–25.00   | 2.12–25.00   | 1.98–26.40   |
| Limiting indices   | –11 ≤ <i>h</i> ≤ 11, –12 ≤<br><i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 16 | –12 ≤ <i>h</i> ≤ 11, –18 ≤<br><i>k</i> ≤ 18, –20 ≤ <i>l</i> ≤ 20 | –11 ≤ <i>h</i> ≤ 11, –12 ≤<br><i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 15 | –14 ≤ <i>h</i> ≤ 14, –15 ≤<br><i>k</i> ≤ 15, –23 ≤ <i>l</i> ≤ 23 |
| Reflections collected  | 22226  | 52298  | 6882   | 46560  |
| Refinement method  | Full-matrix least-squares on <i>F</i> <sup>2</sup>             | Full-matrix least-squares on <i>F</i> <sup>2</sup>               | Full-matrix least-squares on <i>F</i> <sup>2</sup>             | Full-matrix least-squares on <i>F</i> <sup>2</sup>               |
| Data/restraints/parameters                                   | 4754/0/421   | 5120/0/379   | 4079/0/316   | 5391/0/358   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 1.000  | 1.176  | 1.142  | 1.053  |
| Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | <i>R</i> 1 = 0.1132, w <i>R</i> 2 = 0.1033                     | <i>R</i> 1 = 0.1024, w <i>R</i> 2 = 0.1711                       | <i>R</i> 1 = 0.0587, w <i>R</i> 2 = 0.1195                     | <i>R</i> 1 = 0.0321, w <i>R</i> 2 = 0.0582                       |
| <i>R</i> indices (all data)                                  | <i>R</i> 1 = 0.1132, w <i>R</i> 2 = 0.1259                     | <i>R</i> 1 = 0.1544, w <i>R</i> 2 = 0.1933                       | <i>R</i> 1 = 0.0996, w <i>R</i> 2 = 0.1490                     | <i>R</i> 1 = 0.0582, w <i>R</i> 2 = 0.0617                       |
| Largest $\Delta\rho$ (e Å <sup>-3</sup> )                    | 0.175/–0.198   | 0.157/–0.190   | 0.188/–0.213   | 0.155/–0.173   |

Table 2  
Selected bond lengths (Å) and bond angles (°) for **5a**

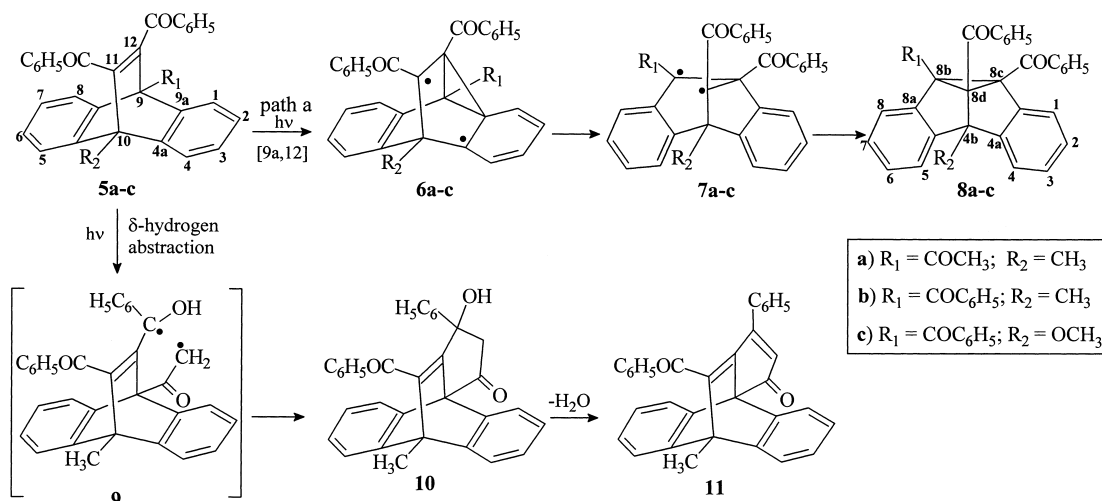
|                    |             |                    |             |
|--------------------|-------------|--------------------|-------------|
| O(1)-C(13)         | 1.213 (2)   | O(2)-C(16)         | 1.221 (2)   |
| O(3)-C(23)         | 1.229 (2)   | C(1)-C(9A)         | 1.387 (2)   |
| C(4A)-C(9A)        | 1.404 (3)   | C(4)-C(4A)         | 1.391 (3)   |
| C(5)-C(10A)        | 1.387 (3)   | C(4A)-C(10)        | 1.539 (3)   |
| C(8)-C(8A)         | 1.389 (3)   | C(8A)-C(10A)       | 1.386 (3)   |
| C(8A)-C(9A)        | 1.547 (3)   | C(9)-C(13)         | 1.529 (3)   |
| C(9)-C(9A)         | 1.547 (3)   | C(9)-C(12)         | 1.550 (3)   |
| C(10)-C(15)        | 1.523 (3)   | C(10)-C(10A)       | 1.532 (3)   |
| C(10)-C(11)        | 1.548 (3)   | C(11)-C(12)        | 1.342 (3)   |
| C(11)-C(16)        | 1.509 (3)   | C(12)-C(23)        | 1.481 (3)   |
| C(9A)-C(1)-C(2)    | 120.0 (2)   | C(3)-C(2)-C(1)     | 120.3 (2)   |
| C(4)-C(4A)-C(9A)   | 120.1 (2)   | C(3)-C(4)-C(4A)    | 119.7 (2)   |
| C(9A)-C(4A)-C(10)  | 114.44 (18) | C(4)-C(4A)-C(10)   | 125.3 (2)   |
| C(7)-C(8)-C(8A)    | 119.6 (3)   | C(8)-C(8A)-C(9)    | 125.9 (2)   |
| C(10A)-C(8A)-C(9)  | 113.6 (18)  | C(13)-C(9)-C(8A)   | 109.08 (17) |
| C(13)-C(9)-C(9A)   | 118.32 (16) | C(13)-C(9)-C(12)   | 113.85 (16) |
| C(9A)-C(9)-C(8A)   | 104.86 (16) | C(18)-C(9)-C(12)   | 106.47 (15) |
| C(9A)-C(9)-C(12)   | 103.31 (15) | C(1)-C(9A)-C(9)    | 128.12 (19) |
| C(1)-C(9A)-C(4A)   | 119.4 (2)   | C(15)-C(10)-C(10A) | 114.17 (19) |
| C(4A)-C(9A)-C(9)   | 112.35 (17) | C(10A)-C(10)-C(4A) | 105.84 (17) |
| C(15)-C(10)-C(4A)  | 113.8 (2)   | C(10A)-C(10)-C(11) | 105.32 (17) |
| C(15)-C(10)-C(11)  | 114.43 (19) | C(8A)-C(10A)-C(5)  | 119.2 (2)   |
| C(4A)-C(10)-C(11)  | 102.62 (15) | C(5)-C(10A)-C(10)  | 125.9 (2)   |
| C(8A)-C(10A)-C(10) | 114.04 (17) | C(12)-C(11)-C(10)  | 115.42 (18) |
| C(12)-C(11)-C(16)  | 127.27 (19) | C(11)-C(12)-C(23)  | 124.76 (19) |
| C(16)-C(11)-C(10)  | 116.85 (17) | C(23)-C(12)-C(9)   | 118.65 (17) |
| C(11)-C(12)-C(9)   | 113.73 (18) | O(1)-C(13)-C(9)    | 122.06 (19) |
| O(1)-C(13)-C(14)   | 119.3 (2)   | O(2)-C(16)-C(17)   | 122.52 (2)  |
| O(2)-C(16)-C(11)   | 118.95 (19) | C(17)-C(16)-C(11)  | 118.39 (17) |
| O(23)-C(23)-C(12)  | 175.45 (19) | C(22)-C(17)-C(16)  | 122.0 (2)   |
| C(12)-C(23)-C(24)  | 122.05 (17) | O(3)-C(23)-C(24)   | 120.50 (18) |

Table 3  
Selected bond lengths (Å) and bond angles (°) for **8c**

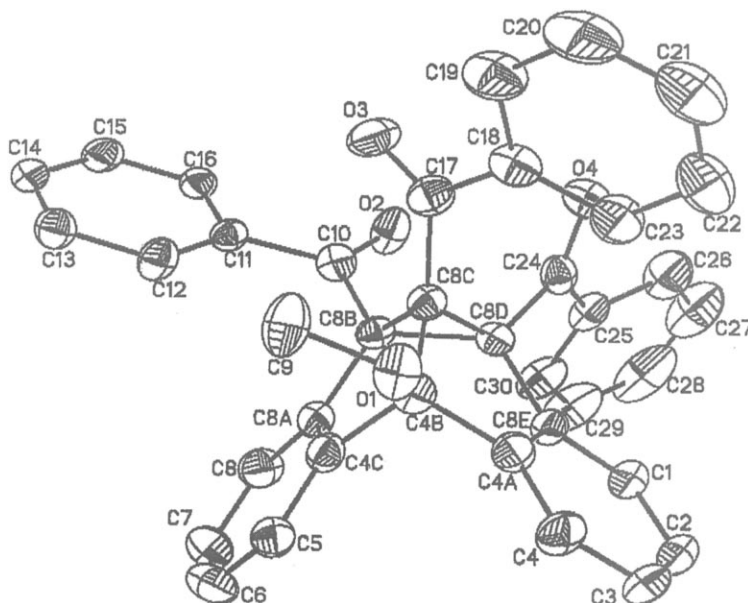
|                   |           |                   |            |
|-------------------|-----------|-------------------|------------|
| O(1)-C(4B)        | 1.399 (6) | C(8C)-C(17)       | 1.515 (8)  |
| O(1)-C(9)         | 1.440 (7) | C(8D)-C(8E)       | 1.509 (7)  |
| O(2)-C(10)        | 1.208 (6) | C(8D)-C(24)       | 1.528 (7)  |
| O(3)-C(17)        | 1.200 (6) | C(10)-C(11)       | 1.503 (7)  |
| O(4)-C(24)        | 1.205 (6) | C(11)-C(12)       | 1.386 (7)  |
| C(4A)-C(8E)       | 1.412 (8) | C(17)-C(18)       | 1.517 (8)  |
| C(4A)-C(4B)       | 1.487 (7) | C(18)-C(19)       | 1.377 (8)  |
| C(4B)-C(4C)       | 1.532 (7) | C(18)-C(23)       | 1.389 (8)  |
| C(4B)-C(8C)       | 1.597 (7) | C(19)-C(20)       | 1.396 (10) |
| C(8A)-C(8B)       | 1.496 (7) | C(26)-C(27)       | 1.420 (13) |
| C(8B)-C(8C)       | 1.515 (7) | C(27)-C(28)       | 1.374 (14) |
| C(8B)-C(10)       | 1.516 (7) | C(28)-C(29)       | 1.334 (14) |
| C(4B)-O(1)-C(9)   | 114.2 (4) | C(5)-C(4C)-C(8A)  | 120.5 (5)  |
| C(2)-C(1)-C(8E)   | 119.2 (6) | C(5)-C(4C)-C(4B)  | 128.0 (5)  |
| C(8E)-C(4A)-C(4B) | 110.9 (4) | C(16)-C(11)-C(10) | 117.1 (5)  |
| O(1)-C(4B)-C(4A)  | 113.9 (4) | C(13)-C(12)-C(11) | 120.0 (5)  |
| O(1)-C(4B)-C(4C)  | 116.8 (5) | C(12)-C(13)-C(14) | 120.7 (5)  |
| C(4A)-C(4B)-C(4C) | 102.6 (4) | C(15)-C(14)-C(13) | 119.2 (5)  |
| O(1)-C(4B)-C(8C)  | 116.1 (5) | C(16)-C(15)-C(14) | 121.0 (5)  |
| C(4A)-C(4B)-C(8C) | 102.6 (4) | C(15)-C(16)-C(11) | 120.1 (5)  |
| C(4C)-C(4B)-C(8C) | 102.9 (4) | O(3)-C(17)-C(8C)  | 120.8 (5)  |
| C(8)-C(8A)-C(8B)  | 128.5 (5) | C(8C)-C(17)-C(18) | 117.4 (5)  |
| C(8A)-C(8B)-C(8C) | 107.4 (4) | C(19)-C(18)-C(17) | 117.8 (6)  |
| C(8C)-C(8B)-C(8D) | 58.4 (3)  | C(21)-C(20)-C(19) | 120.1 (8)  |
| C(8D)-C(8C)-C(8B) | 63.1 (3)  | C(22)-C(23)-C(18) | 120.1 (7)  |
| C(8D)-C(8C)-C(4B) | 104.4 (4) | O(4)-C(24)-C(8D)  | 120.8 (5)  |
| C(8B)-C(8C)-C(4B) | 105.2 (4) | C(30)-C(25)-C(26) | 119.1 (7)  |
| C(8E)-C(8D)-C(8C) | 106.7(4)  | C(30)-C(25)-C(24) | 122.5 (6)  |
| C(8E)-C(8D)-C(24) | 116.6 (4) | C(26)-C(25)-C(24) | 118.4 (7)  |
| C(8C)-C(8D)-C(8B) | 58.5 (3)  | C(29)-C(28)-C(27) | 122.0 (11) |

of **8a**, for example showed two singlets at  $\delta$  1.67 and 2.58, which were assigned to the methyl and acetyl protons, respectively. The structure of a representative example of the photoproduct, **8c** (Fig. 2) was further confirmed through X-ray crystal structure determination [26] (Table 3). The structure of the photoproduct **11** was also confirmed through X-ray crystallographic analysis [26] (Table 4, Fig. 3).

Interestingly, the dibenzosemibullvalene **8a** derived from the 9-acetyl-10-methyldibenzobarrelene **5a**, underwent a facile reaction with methanol to give an acetal derivative **15**, in quantitative yields (Scheme 3). In contrast, the benzoyl substituted semibullvalene derivatives **8b** and **8c** were found to be quite stable in methanol, even under reflux conditions. The structure of **15** (Fig. 4) was unambiguously established through X-ray crystallographic analysis [26] (Table 5).



Scheme 2.

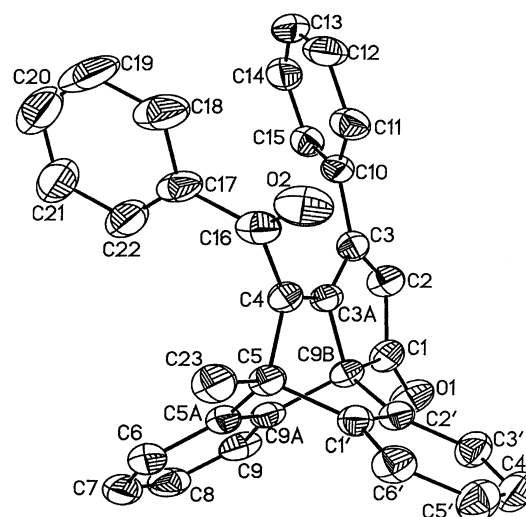
Fig. 2. Projection view of **8c** with 30% probability ellipsoids.Table 4  
Selected bond lengths (Å) and bond angles (°) for **11**

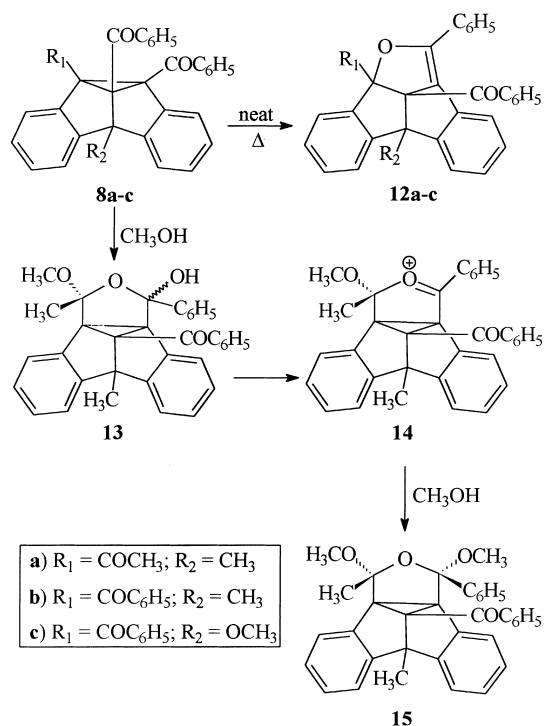
|                   |             |                   |           |
|-------------------|-------------|-------------------|-----------|
| O(1)-C(1)         | 1.222 (2)   | O(2)-C(16)        | 1.227 (4) |
| C(1)-C(2)         | 1.464 (4)   | C(1)-C(9B)        | 1.524 (2) |
| C(2)-C(3)         | 1.365 (4)   | C(3)-C(3A)        | 1.472 (4) |
| C(3A)-C(9B)       | 1.532 (3)   | C(3A)-C(4)        | 1.342 (4) |
| C(4)-C(5)         | 1.569 (4)   | C(4)-C(16)        | 1.505 (3) |
| C(5)-C(5A)        | 1.538 (4)   | C(5)-C(1')        | 1.543 (4) |
| C(5A)-C(6)        | 1.392 (4)   | C(5A)-C(9A)       | 1.405 (4) |
| C(9A)-C(9B)       | 1.537 (4)   | C(9B)-C(2')       | 1.531 (3) |
| C(16)-C(17)       | 1.488 (4)   | C(18)-C(19)       | 1.405 (6) |
| C(1')-C(2')       | 1.509 (3)   | C(4')-C(5')       | 1.379 (4) |
| O(1)-C(1)-C(2)    | 126.9 (3)   | O(1)-C(1)-C(9B)   | 126.0 (3) |
| C(2)-C(1)-C(9B)   | 107.1 (2)   | C(3)-C(2)-C(1)    | 111.8 (2) |
| C(2)-C(3)-C(3A)   | 109.6 (2)   | C(2)-C(3)-C(10)   | 125.5 (2) |
| C(3A)-C(3)-C(10)  | 124.7 (2)   | C(4)-C(3A)-C(3)   | 137.3 (2) |
| C(4)-C(3A)-C(9B)  | 114.8 (2)   | C(3)-C(3A)-C(9B)  | 107.9 (2) |
| C(3A)-C(4)-C(16)  | 128.5 (2)   | C(3A)-C(4)-C(5)   | 113.0 (2) |
| C(16)-C(4)-C(5)   | 118.3 (2)   | C(23)-C(5)-C(5A)  | 113.7 (2) |
| C(23)-C(5)-C(1')  | 114.3 (2)   | C(5A)-C(1)-C(1')  | 104.2 (2) |
| C(23)-C(5)-C(4)   | 113.2 (2)   | C(5A)-C(5)-C(4)   | 104.8 (2) |
| C(1')-C(5)-C(4)   | 105.6 (2)   | C(6)-C(5A)-C(9A)  | 119.5 (3) |
| C(6)-C(5A)-C(5)   | 126.7 (3)   | C(9A)-C(5A)-C(5)  | 113.8 (2) |
| C(9)-C(9A)-C(5A)  | 121.0 (3)   | C(9)-C(9A)-C(9B)  | 127.0 (3) |
| C(5A)-C(9A)-C(9B) | 111.9 (2)   | C(5)-C(10A)-C(10) | 125.9 (2) |
| C(1)-C(9B)-C(3A)  | 103.6(2)    | C(1)-C(9B)-C(2')  | 117.2 (2) |
| C(1)-C(9B)-C(9A)  | 116.6(2)    | C(2')-C(9B)-C(3A) | 107.1 (2) |
| C(3A)-C(9B)-C(9A) | 106.1 (2)   | C(2')-C(9B)-C(9A) | 104.8 (2) |
| O(2)-C(16)-C(4)   | 118.1 (3)   | O(2)-C(16)-C(17)  | 122.6 (3) |
| C(18)-C(17)-C(16) | 118.7 (3)   | C(17)-C(18)-C(19) | 118.6 (4) |
| C(20)-C(19)-C(18) | 118.95 (19) | C(6')-C(1')-C(5)  | 126.3 (2) |
| C(2')-C(1')-C(5)  | 113.8 (2)   | C(1')-C(2')-C(9B) | 112.1 (2) |
| C(3')-C(2')-C(9B) | 126.7 (2)   | C(1')-C(6')-C(5') | 118.9 (3) |

#### 4.2. Thermal transformations of dibenzosemibullvalene derivatives **8a–c** to dibenzopentalenofurans **12a–c**

The dibenzosemibullvalenes **8a–c**, formed as primary photo-products from **5a–c** were found to be thermally unstable and

they underwent isomerization to the corresponding dibenzopentalenofuran derivatives (Scheme 3). For example, neat heating of **8a** for 2 h at 180–200°C gave **12a** in a 92% yield. Similarly, the thermolysis of semibullvalenes **8b** and **8c**, under identical conditions, yielded the corresponding semibullvalenes **12b** (95%) and **12c** (87%), respectively. The <sup>13</sup>C NMR spectrum of **12a** showed characteristic five sp<sup>3</sup> carbons at δ 21.5, 28.96, 60.07, 89.24 and 103.13 and two carbonyl peaks at δ 200.29 and 205.36, indicating thereby the participation of one of the benzoyl groups in the furan ring formation. The kinetics of thermal isomerization of **8a–c** to **12a–c** was studied by UV spectroscopy. The activation and thermodynamic parameters observed for these thermal isomerizations are summarized in Table 6.

Fig. 3. Projection view of **11** with 50% probability ellipsoids.



Scheme 3.

## 5. Discussion

The formation of the dibenzosemibullvalenes **8a–c** in the phototransformations of **5a–c** can be rationalized in terms of the pathway shown in Scheme 2. Path ‘a’ involves a [9,12] benzo-vinyl bridging leading to the diradical intermediates **6a–c** and **7a–c**, which can subsequently undergo transformations to the products **8a–c**. The observed regioselectivity in these reactions could be directly correlated to the relative stabilities of the 1,3-diradical intermediates **6a–c** and **7a–c**. The diradical intermediates **7a–c**, wherein the bridgehead substituents are directly

attached to the radical center (for a review on steric effects in free radical chemistry, see [27]), could be stabilized by the benzoyl and acetyl groups through delocalization, [28] thereby leading to the preferred formation of *8b*-substituted semibullvalenes. It must be mentioned here that 9-benzoyl substituted dibenzobarrelene, [29,30] on irradiation gave the corresponding *8b*-substituted semibullvalene derivative, whereas 9-methyl and 9-methoxy substituted dibenzobarrelenes gave the *4b*-substituted semibullvalenes. On the other hand, photolysis of the 9-acetyldibenzobarrelene [25] gave a mixture of the *4b* and *8b* isomers in 70 and 20% yields, respectively. Results of our earlier studies [29–32] with mono-substituted dibenzobarrelenes, in general, indicate that electron-withdrawing substituents favor the *8b*-substituted products, whereas electron-donating substituents such as methyl and methoxy groups give the corresponding *4b*-substituted dibenzosemibullvalenes. Therefore, the formation of regioselective dibenzosemibullvalenes **8a–c** from **5a–c**, could be attributed to the combined effects of these two types of substituents.

The formation of the polycyclic ketone **11**, which arises through a different mode of reaction of the starting 9-acetyl-10-methyldibenzobarrelene (**5a**), could be rationalized in terms of the pathway shown in Scheme 2 (path b). The excited state of **5a** can abstract a  $\delta$ -hydrogen atom from the adjacent methyl group of the acetyl substituent to give the 1,5-biradical intermediate **9** (for a review on 1,5-biradicals generated by  $\delta$ -hydrogen abstraction see [33]), which can subsequently couple to give the carbinol derivative **10**. Elimination of water from **10** will lead to the observed product **11**. The formation of polycyclic ketone **11** shows that the bridgehead substituents have a bearing in controlling the reaction pathways of the starting dibenzobarrelenes. It is interesting to note that only in the disubstituted derivative **5a** such a pathway involving hydrogen atom abstraction from the acetyl substituent was observed. The mono-substituted 9-acetyldibenzobarrelene, on the other hand, yielded, on irradiation a mixture of the *4b* and *8b*-substituted dibenzosemibullvalenes, and no product derived through hydrogen abstraction from the acetyl group could be observed [25]. It may be pointed out here that X-ray crystallographic analysis [26] of the dibenzobarrelene **5a** (Fig. 1) has revealed that the hydrogen atom of the acetyl group and the oxygen atom of the adjacent benzoyl group are in close proximity (2.75 Å, Fig. 1) so as to favor the formation of **9**, through a  $\delta$ -hydrogen atom abstraction and ultimately leading to the formation of product **11**.

In the formation of the acetal derivative **15**, it is assumed that methanol adds to the acetyl carbonyl to give a hemiacetal, which can subsequently add to the benzoyl carbonyl group to give the intermediate hemiacetal derivative **13**. Elimination of water from **13** would lead to the oxonium intermediate **14**, which can further add methanol to give exclusively the *cis*-acetal derivative **15** (Fig. 4).

The thermal isomerizations of the dibenzosemibullvalenes **8a–c** to the corresponding dibenzopentalenofurans

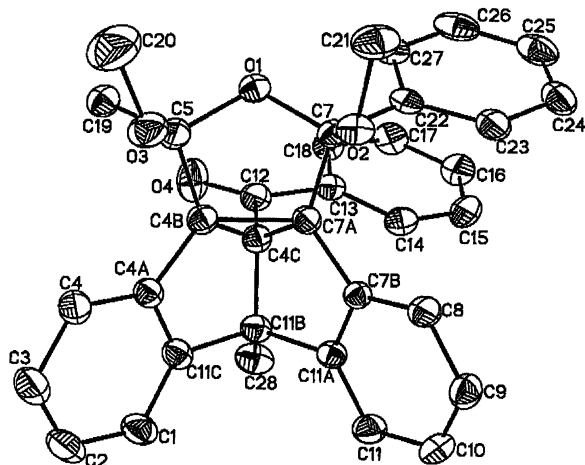
Fig. 4. Projection view of **15** with 50% probability ellipsoids.



Table 5  
Selected bond lengths (Å) and bond angles (°) for **15**

|                    |             |                      |             |
|--------------------|-------------|----------------------|-------------|
| O(1)-C(7)          | 1.4302 (17) | C(7A)-C(7B)          | 1.4921 (19) |
| O(1)-C(5)          | 1.4440 (18) | C(7B)-C(8)           | 1.3836 (19) |
| O(2)-C(7)          | 1.4196 (18) | C(7B)-C(11A)         | 1.394 (2)   |
| O(2)-C(21)         | 1.4364 (18) | C(8)-C(9)            | 1.384 (2)   |
| O(3)-C(5)          | 1.4167 (19) | C(9)-C(10)           | 1.381 (2)   |
| O(3)-C(20)         | 1.424 (2)   | C(10)-C(11)          | 1.380 (2)   |
| O(4)-C(12)         | 1.2170 (18) | C(11)-C(11A)         | 1.380 (2)   |
| C(1)-C(2)          | 1.385 (2)   | C(11A)-C(11B)        | 1.525 (2)   |
| C(1)-C(11C)        | 1.387 (2)   | C(11B)-C(28)         | 1.521 (2)   |
| C(4A)-C(4B)        | 1.484 (2)   | C(14)-C(15)          | 1.384 (2)   |
| C(4B)-C(5)         | 1.510 (2)   | C(15)-C(16)          | 1.375 (2)   |
| C(4B)-C(4C)        | 1.518 (2)   | C(16)-C(17)          | 1.375 (2)   |
| C(4B)-C(7A)        | 1.579 (2)   | C(17)-C(18)          | 1.372 (2)   |
| C(4C)-C(7A)        | 1.516 (2)   | C(22)-C(23)          | 1.386 (2)   |
| C(4C)-C(12)        | 1.516 (2)   | C(22)-C(27)          | 1.388 (2)   |
| C(4C)-C(11B)       | 1.582 (2)   | C(23)-C(24)          | 1.386 (2)   |
| C(7)-C(7A)         | 1.520 (2)   | C(26)-C(27)          | 1.396 (2)   |
| C(7)-O(1)-C(5)     | 110.22 (10) | C(11C)-C(4A)-C(4B)   | 109.46 (14) |
| C(7)-O(2)-C(21)    | 114.70 (12) | C(4A)-C(4B)-C(5)     | 124.86 (13) |
| C(5)-O(3)-C(20)    | 117.86 (14) | C(4A)-C(4B)-C(4C)    | 108.17 (12) |
| C(4)-C(3)-C(2)     | 121.09 (18) | C(5)-C(4B)-C(7A)     | 105.38 (12) |
| C(3)-C(4)-C(4A)    | 119.19 (16) | C(4C)-C(4B)-C(7A)    | 58.58 (9)   |
| C(4)-C(4A)-C(11C)  | 119.77 (14) | C(7A)-C(4C)-C(12)    | 129.90 (13) |
| C(4)-C(4A)-C(4B)   | 130.76 (15) | C(7A)-C(4C)-C(4B)    | 62.73 (10)  |
| C(12)-C(4C)-C(4B)  | 127.11 (13) | C(11A)-C(11B)-C(11C) | 101.76 (11) |
| C(12)-C(4C)-C(11B) | 115.90 (13) | C(11A)-C(11B)-C(4C)  | 102.40 (12) |
| C(4B)-C(4C)-C(11B) | 104.57 (11) | C(11C)-C(11B)-C(4C)  | 102.65 (12) |
| O(3)-C(5)-O(1)     | 110.79 (13) | C(1)-C(11C)-C(4A)    | 120.82 (16) |
| O(3)-C(5)-C(19)    | 112.04 (13) | C(1)-C(11C)-C(11B)   | 127.35 (15) |
| O(1)-C(5)-C(19)    | 107.60 (13) | C(4A)-C(11C)-C(11B)  | 111.37 (13) |
| O(3)-C(5)-C(4B)    | 104.53 (12) | O(4)-C(12)-C(13)     | 120.39 (14) |
| O(1)-C(5)-C(4B)    | 104.42 (12) | O(4)-C(12)-C(4C)     | 119.79 (14) |
| O(2)-C(7)-O(1)     | 111.62 (12) | C(14)-C(13)-C(18)    | 118.88 (15) |
| O(2)-C(7)-C(22)    | 110.29 (12) | C(14)-C(13)-C(12)    | 122.30 (14) |

are analogues to the rearrangement of vinylcyclopropanes to cyclopentenes, reported in the literature [34,35]. These isomerizations could proceed either through a concerted pathway, involving a [1,3] sigmatropic shift or through 1,3-diradical intermediates [36–38]. Though the activation energy [35] for the rearrangement of vinylcyclopropane to cyclopentene is 45 kcal mol<sup>-1</sup>, it is established that increased carbon substitution, extended conjugation, or the

presence of heteroatom lower the activation energy for the reorganization towards cyclopentene [34–38]. Our kinetic studies reveal that the isomerizations of **8a–c** follow first order kinetics, as expected. The activation energy for the thermal isomerization of **8a–12a**, for example, was found to be 21.04 kcal mol<sup>-1</sup> and the change in entropy of activation was -18.43 eu, which is typical of sigmatropic rearrangements involving cyclic transition states [39–41]. It is interesting

Table 6  
Kinetic and thermodynamic data for the thermal isomerization of **8a**, **8b** and **8c**<sup>a</sup>

| Thermal isomerization <sup>b</sup> | Temperature (K) | Rate constant <i>k</i> , 10 <sup>-3</sup> sec | <i>E</i> <sub>a</sub> (kcal mol <sup>-1</sup> ) | Δ <i>S</i> <sup>#</sup> (eu) |
|------------------------------------|-----------------|---|---|------------------------------|
| <b>8a–12a</b>                      | 383             | 1.73  | 21.04 ± 0.51                                    | -18.43                       |
|                                    | 388             | 2.52  |   |                              |
|                                    | 393             | 3.51  |   |                              |
| <b>8b–12b</b>                      | 413             | 1.18  | 23.42 ± 0.63                                    | -17.55                       |
|                                    | 418             | 1.70  |   |                              |
|                                    | 423             | 2.40  |   |                              |
| <b>8c–12c</b>                      | 413             | 1.27  | 24.74 ± 0.98                                    | -16.14                       |
|                                    | 418             | 1.94  |   |                              |
|                                    | 423             | 2.66  |   |                              |

<sup>a</sup> Average of more than two experiments.

<sup>b</sup> The thermal isomerization monitoring wavelengths (λ<sub>max</sub>) are 324 nm for **8a–12a**, 321 nm for **8b–12b** and 321 nm for **8c–12c**.

to note that the activation energy for the thermal isomerization of **8b** and **8c** is higher than that of **8a** (Table 6). This difference, albeit small could be attributed to the electronic effects of the substituents present on the cyclopropane ring.

### Acknowledgements

We (M.C.S., D.R., M.M., M.V.G) thank the Council of Scientific and Industrial Research, Department of Science and Technology, Government of India, the Volkswagen Foundation, Germany (D.R.), the University of Missouri-St. Louis (N.P.R.) and Jawarharlal Nehru Centre for Advanced Scientific Research, Bangalore (M.V.G.) for financial support of this work.

### References

- [1] H.E. Zimmerman, in: P. de Mayo (Ed.), *Rearrangements in Ground and Excited States*, Academic Press, New York, Vol. 3, Chapter 16, 1980, pp. 131–166.
- [2] H.E. Zimmerman, in: A. Padwa (Ed.), *Organic Photochemistry*, Marcel Dekker, New York, Vol. 11, 1991, pp. 1–36.
- [3] O. de Lucchi, W. Adam, in: B.M. Trost, L.A. Paquette (Eds.), *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, Vol. 5, 1991, pp. 193–214.
- [4] H.E. Zimmerman, H.M. Sulzbach, M.B. Tollefson, *J. Am. Chem. Soc.* 115 (1993) 6548–6556.
- [5] J.R. Scheffer, J. Yang, in: W.M. Horspool, P.S. Song (Eds.), *CRC Handbook of Organic Photochemistry and Photobiology*, CRC Press, Boca Raton, FL, Chapter 16, 1995, pp. 204–221.
- [6] A.R. Katritzky, C.W. Reed, in: C.W. Bird, G.W.H. Cheeseman (Eds.), *Comprehensive Heterocyclic Chemistry*, Pergamon Press, Oxford, Vol. 4, Part 3, Chapter 12, 1984, pp. 657–712.
- [7] E. Ciganek, *J. Am. Chem. Soc.* 88 (1966) 2882–2883.
- [8] P.W. Rabideau, J.B. Hamilton, L. Friedmann, *J. Am. Chem. Soc.* 90 (1968) 4465–4465.
- [9] H.E. Zimmerman, G.L. Grunewald, *J. Am. Chem. Soc.* 88 (1966) 183–184.
- [10] H.E. Zimmerman, R.W. Binkley, R.S. Givens, M.A. Sherwin, *J. Am. Chem. Soc.* 89 (1967) 3932–3933.
- [11] P.R. Pokkuluri, J.R. Scheffer, J. Trotter, *J. Am. Chem. Soc.* 112 (1990) 3675–3676.
- [12] J. Chen, P.R. Pokkuluri, J.R. Scheffer, J. Trotter, *J. Photochem. Photobiol. A: Chem.* 7 (1991) 21–26.
- [13] M. Iwamura, H. Tukada, H. Iwamura, *Tetrahedron Lett.* 21 (1980) 4865–4868.
- [14] C.V. Kumar, B.A.R.C. Murthy, S. Lahiri, E. Chackachery, J.C. Scaiano, M.V. George, *J. Org. Chem.* 49 (1984) 4923–4929.
- [15] S.A. Kumar, C.V. Ashokan, S. Das, J.A. Wilbur, N.P. Rath, M.V. George, *J. Photochem. Photobiol. A: Chem.* 71 (1993) 27–31.
- [16] D. Ramaiah, S.A. Kumar, C.V. Ashokan, T. Mathew, S. Das, N.P. Rath, M.V. George, *J. Org. Chem.* 61 (1996) 5468–5473.
- [17] C.V. Ashokan, S.A. Kumar, S. Das, N.P. Rath, M.V. George, *J. Org. Chem.* 56 (1991) 5890–5893.
- [18] D. Ramaiah, M. Muneer, K.R. Gopidas, P.K. Das, N.P. Rath, M.V. George, *J. Org. Chem.* 61 (1996) 4240–4246.
- [19] D. Ramaiah, K. Ashok, R. Barik, D. Venugopal, N.P. Rath, K. Bhattacharyya, P.K. Das, M.V. George, *J. Org. Chem.* 57 (1992) 6032–6037.
- [20] R.E. Lutz, in: E.C. Horning (Ed.), *Organic Synthesis*, Wiley, New York, Collected Vol. 3, 1995, pp. 248–250.
- [21] R.E. Lutz, W.R. Smithy Jr., *J. Org. Chem.* 16 (1951) 648–654.
- [22] C. Merritt Jr., C.E. Braun, in: N. Rabjohn (Ed.), *Organic Synthesis*, Wiley, New York, Collected Vol. 4, 1967, pp. 8–10.
- [23] A.I. Bokava, I.K. Buchina, *Zh. Org. Khim.* 20 (1984) 1318–1321.
- [24] F. Krollpfeiffer, F. Branschield, F. Thorn, K. Schneider, *Annals* 462 (1928) 46–72.
- [25] M.C. Sajimon, D. Ramaiah, M. Muneer, E.S. Ajithkumar, N.P. Rath, M.V. George, *J. Org. Chem.* 64 (1999) 6347–6352.
- [26] G.M. Sheldrick, Siemens Analytical X-ray Division, Madison, WI, 1991.
- [27] C. Rüchardt, *Top. Curr. Chem.* 88 (1980) 1–32.
- [28] L.A. Paquette, E. Bay, *J. Am. Chem. Soc.* 106 (1984) 6693–6701.
- [29] B.A.R.C. Murthy, S. Pratapan, C.V. Kumar, P.K. Das, M.V. George, *J. Org. Chem.* 50 (1985) 2533–2538.
- [30] S.A. Kumar, D. Ramaiah, N.V. Eldho, S. Das, N.P. Rath, M.V. George, *J. Photochem. Photobiol. A: Chem.* 103 (1997) 69–73.
- [31] S. Pratapan, K. Ashok, D.R. Cyr, P.K. Das, M.V. George, *J. Org. Chem.* 52 (1987) 5512–5517.
- [32] C.V. Ashokan, S.A. Kumar, S. Das, N.P. Rath, M.V. George, *J. Org. Chem.* 56 (1991) 5890–5893.
- [33] P.J. Wagner, *Acc. Chem. Res.* 22 (1989) 83–92.
- [34] E. Wenkert, *Acc. Chem. Res.* 13 (1980) 27–31.
- [35] T. Hudlicky, J.W. Reed, in: B.M. Trost, L.A. Paquette (Eds.), *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, Vol. 5, 1991, pp. 899–970.
- [36] D. Griller, K.U. Ingold, *Acc. Chem. Res.* 13 (1980) 317–323.
- [37] J.J. Gajewski, L.P. Olson, M.R. Willcott, *J. Am. Chem. Soc.* 118 (1996) 299–306.
- [38] J.E. Baldwin, K.A. Villarica, D.I. Freedberg, F.A.L. Anet, *J. Am. Chem. Soc.* 116 (1994) 10845–10846.
- [39] M. Szwarc, J. Murawski, *Soc. Faraday Trans.* 47 (1951) 269–274.
- [40] F.W. Schuler, G.W. Murphy, *J. Am. Chem. Soc.* 72 (1950) 3155–3159.
- [41] R.N. Haszeldine, P.J. Robinson, J.A. Walsh, *J. Chem. Soc. B* (1970) 578.