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Journal of Photochemistry and Photobiology A: Chemistry 95 (1996) 137–141

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Phototransformations of 9-ethyl-substituted dibenzobarrelene ☆

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Received 22 September 1995; accepted 13 October 1995

Abstract

Photolysis of 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (**1**) in benzene or acetone in the complete absence of oxygen gives the 4b-ethyl-substituted dibenzosemibullvalene (**5**) (45–48%) whereas, in the presence of oxygen, **1** in acetone gives a mixture of **5** (32%), together with two oxygenated products, namely the peroxy compound **12** and the lactone **20**. The structures of **5**,**12** and **20** have been confirmed through single-crystal X-ray diffraction studies. Compound **5** arises through a di-π-methane rearrangement of **1**, whereas **12** is formed through the oxygen quenching of a diradical intermediate, derived from an isomeric 8b-ethyl-substituted dibenzosemibullvalene (**6**). Compound **20** arises through the oxygen quenching of a diradical intermediate, implicated in the photorearrangements of 1,2-dibenzoylalkenes.

Keywords: Phototransformations; Dibenzosemibullvalenes; X-ray diffraction; Oxygen-quenching

1. Introduction

Earlier, we reported the results of our studies on the phototransformations of several bridgehead monosubstituted dibenzobarrelenes including that of 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (**1**) [1]. It has been observed that the photolysis of **1** leads to a mixture of products, depending on the reaction conditions. Thus the photolysis of **1** in benzene gives rise to a mixture of a 4b-ethyl-substituted dibenzosemibullvalene and an oxygenated product, whereas the irradiation of **1** in acetone gives the same dibenzosemibullvalene and on oxygenated derivative, together with a small yield of a lactonic product. On the basis of well-established pathways for the phototransformations of benzo and naphthobarrelene derivatives [1], it has been suggested that the observed photoproducts from **1** arise through a triplet-state-mediated di-π-methane rearrangement, leading to the corresponding dibenzosemibullvalene and that the oxygenated derivative may be formed from the dibenzosemibullvalene precursor. In a recent reinvestigation [3] of the structures of the photoproducts derived from 9,10-dimethyl-substituted dibenzobarrelene through X-ray crystallographic analysis, it has been shown that they have structures quite different from those inferred earlier on the basis of simple triplet-state-mediated di-π-methane rearrangement. The observed photoproducts are better rationalized in terms of 1,4-diradical intermediates, formed through a tri-π-methane pathway [4] and also 1,3-diradical intermediates derived from the initially formed dibenzosemibullvalene through a di-π-methane route. This prompted us to reinvestigate the photochemistry of **1** and to examine the structures of the photoproducts through X-ray crystallographic analysis.

2. Experimental details

The equipment and procedure for melting-point (m.p.) determination and spectral recordings have been described in an earlier publication [5]. Nuclear magnetic resonance (NMR) spectra were recorded on either a JEOL EX-90 or a Varian EM-360 NMR spectrometer and mass spectra were recorded on a Finnigan MAT Model 8430 or JEOL JMS AX505HA mass spectrometer. All steady state irradiation experiments were carried out in a Srinivasan–Griffin–Rayonet photochemical reactor (RPR 3000 Å) 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 boiling point 60–80 °C.

☆ Contribution NDRL-3743 from the Notre Dame Radiation Laboratory and Contribution RRLT-PRU-50 from the Regional Research Laboratory, Trivandrum.

[1] For some pertinent references, see [2].

1010-6030/96/$15.00
SSDI 1010-6030(95)04254-7

2.1. Starting materials

The starting dibenzobarrelene, namely 11,12-dibenzoyl-9-ethyl-9,10-dihydro-9,10-ethenoanthracene (**1**) [6] (m.p., 217–219 °C), was prepared by a reported procedure.

2.2. Irradiation of 1 in the absence of oxygen

A solution of **1** (500 mg, 1.14 mmol) in acetone (350 ml) was irradiated using a Hanovia 450 W medium pressure mercury vapor lamp for 1 h. The solvent was removed under reduced pressure and the resultant residue was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether afforded 240 mg (48%) of 8b,8c-dibenzoyl-4b-ethyl-4b,8b,8c,8d-tetrahydrodibenzo-[a,f]cyclopropa[c,d]-pentalene (**5**) [1] (m.p., 192–193 °C) (mixture m.p.).

Continued elution with a mixture (1:1) of benzene and petroleum ether gave 110 mg (22%) of the unchanged **1** (m.p., 217–218 °C) (mixture m.p.).

In a repeat run, a benzene solution of **1** (500 mg, 1.14 mmol in 350 ml) was irradiated for 1 h and worked up under identical conditions to give 225 mg (45%) of **5** (m.p., 192–193 °C) (mixture m.p.), together with 115 mg (23%) of unchanged **1** (m.p., 217–219 °C) (mixture m.p.).

2.3. Irradiation of 1 in the presence of oxygen

A solution of **1** (500 mg, 1.14 mmol) in acetone (350 ml) was irradiated for 1 h, after saturating it with oxygen. The reaction mixture, after removal of the solvent under reduced pressure, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 15 mg (5%) of 9-ethyl-9,10-dihydro-9,10-(11-phenoxy-11-phenyl-13-oxo)furanoanthracene (**20**) (m.p., 178–179 °C). IR (KBr): ν_{max}(CH) 3060, 2980, 2920, ν_{max}(C=O) 1750, ν_{max} (C=C) 1645, 1590 cm^{-1}. UV (CH_3OH): λ_{max} (ϵ) 236 (8770), 265 (2030, sh), 272 (1930, sh), 280 (1820, sh) nm. ^{1}H NMR ($CDCl_3$): δ 1.50 (3H, t, CH_3), 2.80 (2H, q, CH_2), 5.1 (1H, s, bridgehead CH), 6.7–7.7 (18H, m, aromatic) ppm. Mass spectrum (fast atom bombardment); *m/z* 457 (MH^+).

Further elution with a mixture (2:3) of benzene and petroleum ether gave 160 mg (32%) of **5** (m.p., 192–193 °C) (mixture m.p.).

Elution was continued with a mixture (1:1) of benzene and petroleum ether to give 50 mg (10%) of the unchanged **1** (m.p., 217–219 °C) (mixture m.p.).

Elution with a mixture (4:1) of benzene and petroleum ether and recrystallization from a mixture (1:1) of methanol and dichloromethane yielded 80 mg (15%) of 8b-benzoyl-8b,14a-endoperoxy-14-methyl-9-oxo-4b,8b,8c,14,14a-pentahydrodibenzo[a,f]-naphtho[2,3-c]pentalene (**12**) (m.p., 224–225 °C). IR (KBr): ν_{max}(CH) 3080, 2980, 2920, ν_{max}(C=O) 1695, 1610 cm^{-1}; UV (CH_3OH): λ_{max} (ϵ) 250 (19 800), 272 (7480, sh), 284 (3420, sh), 316 (490, sh) nm. ^{1}H NMR ($CDCl_3$): δ 0.80 (3H, d, CH_3), 3.55 (1H, q, CH), 5.6 (1H, s, bridgehead CH), 6.9–7.8 (17 H, m, aromatic) ppm. ^{13}C NMR ($CDCl_3$): δ 23.4, 37.0, 54.5, 88.5, 101.0, 122.7–148.0, 196 (C=O), 217 (C=O) ppm. Molecular weight. Found: 470.1506 (high resolution mass spectrometry). $C_{32}H_{22}O_4$ calc.: 470.1518.

In a repeat run, irradiation of a benzene solution of **1** (500 mg, 1.14 mmol in 350 ml) under analogous conditions, followed by work-up in the usual manner gave 160 mg (32%) of **5** (m.p., 192–193 °C) (mixture m.p.), 60 mg (12%) of **1** (m.p., 217–218 °C) (mixture m.p.) and 54 mg (10%) of **12** (m.p., 224–225 °C) (mixture m.p.).

2.4. X-ray structure determination of 5, 12 and 20

Colorless crystals of **5**, **12** and **20** of appropriate dimensions were subjected to X-ray structure determination, employing a Siemens R3 automated four-circle diffractometer. A summary of crystal data and intensity collection parameters is available from the authors. Data reduction, structure solution and refinement were achieved by SHELXTL-PLUS (VMS) structure solution software package [7] [2].

3. Results

3.1. Preparative photochemistry and product identification

Irradiation of **1** in benzene or acetone in the complete absence of oxygen gave the dibenzosemibullvalene **5** (45–48%) whereas, in the presence of oxygen, **1** in acetone gave a mixture of the dibenzosemibullvalene **5** (32%), a lactone derivative **20** (5%) and a peroxy compound **12** (12%) (Schemes 1 and 2). Similarly, the irradiation of **1** in benzene under oxygen saturation gave a mixture of **5** (32%) and **12** (10%). The structures of **5**, **12** and **20** were arrived at on the basis of spectral evidence and confirmed through X-ray crystallographic analysis.

3.2. X-ray structure determination of 5, 12 and 20

Compounds **5** and **12** crystallize in the monoclinic space group $P2_1/n$, whereas **20** crystallized in the triclinic space group $P\bar{1}$. None of the structures (**5**, **12** and **20**) shows any kind of molecular disorder. The projection views of **5**, **12** and **20** are presented in Figs. 1, 2 and 3 respectively.

Compound **5** has a pentacyclic 6,5,3,5,6-member-fused-ring core, with two benzoyl groups at 8b and 8c positions in the cyclopropane ring. The ethyl group is attached to the 4b position. Compound **12** has a heptacyclic structure incorporating a peroxy linkage between 8b and 8d carbon atoms. The

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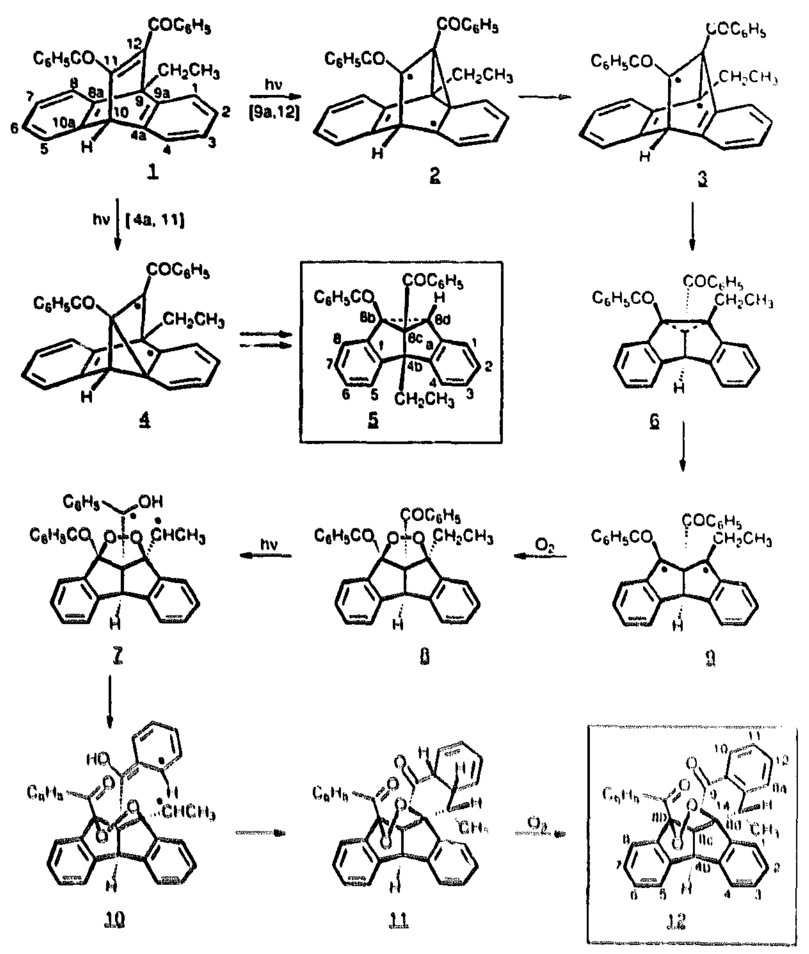
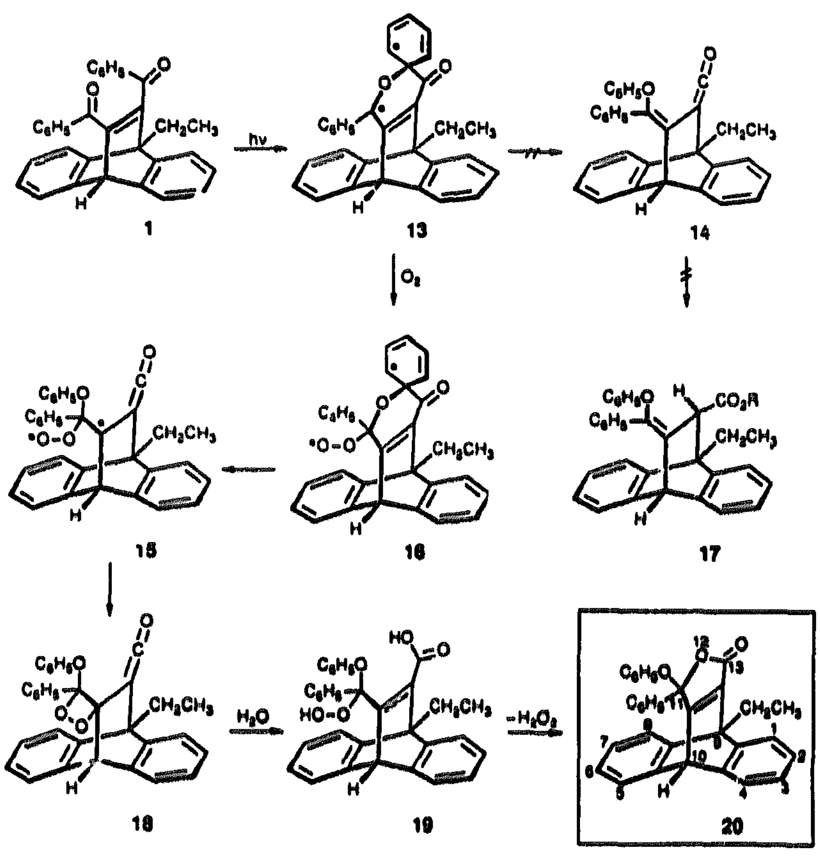
[2] Details of X-ray crystallographic analysis of 5, 12 and 20 including bond distances, bond angles, anisotropic displacement coefficients, H-atom coordinates, isotropic displacement coefficients and list of structure factors will be published separately.



Scheme 1.



Scheme 2.

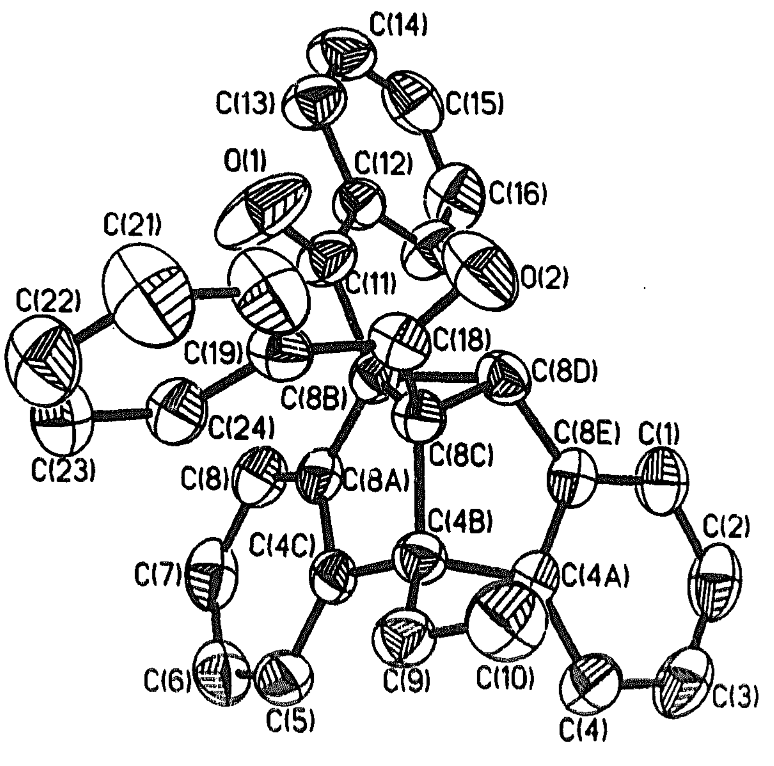


Fig. 1. Projection view of 5 with 50% probability ellipsoids.

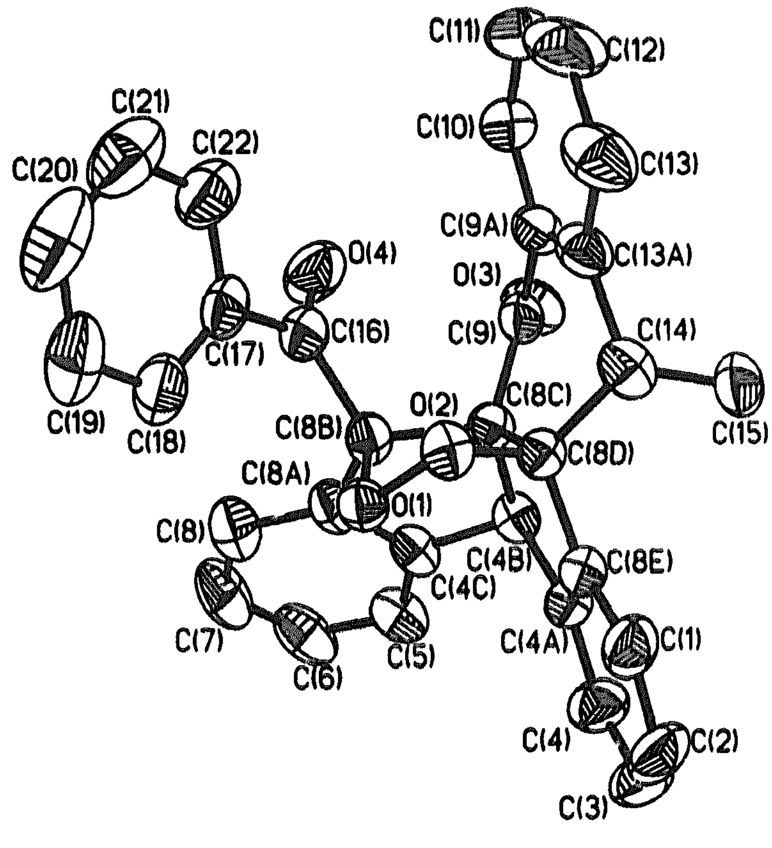


Fig. 2. Projection view of 12 with 50% probability ellipsoids.

O–O distance is 1.466(3) Å and is comparable with the average peroxy distance of 1.464(9) Å [8]. The quaternary carbon 8c makes an angle of 101.1(2)° between 8b and 8d (C(8b)–C(8c)–C(8d)), which is 8.4° less than the tetrahedral angle. This deviation could be due to the formation of the strained endoperoxide ring in 12. Compound 20 incorporates a bicyclo[2·2·2]octa-2,5,7-triene (barrelene) core to which two benzene rings and a lactone ring are fused. The lactone ring is substituted by a phenyl group and a phenoxy group at C(11) position. The ethyl substituent is attached to the bridgehead C(9) carbon as shown in Fig. 3.

4. Discussion

The formation of the dibenzosemibullvalene 5 and the peroxy compound 12 can be rationalized in terms of a di-π-methane pathway as shown in Scheme 1. An initial [9a,12] benzo-vinyl bridging in 1, under photoexcitation, would lead

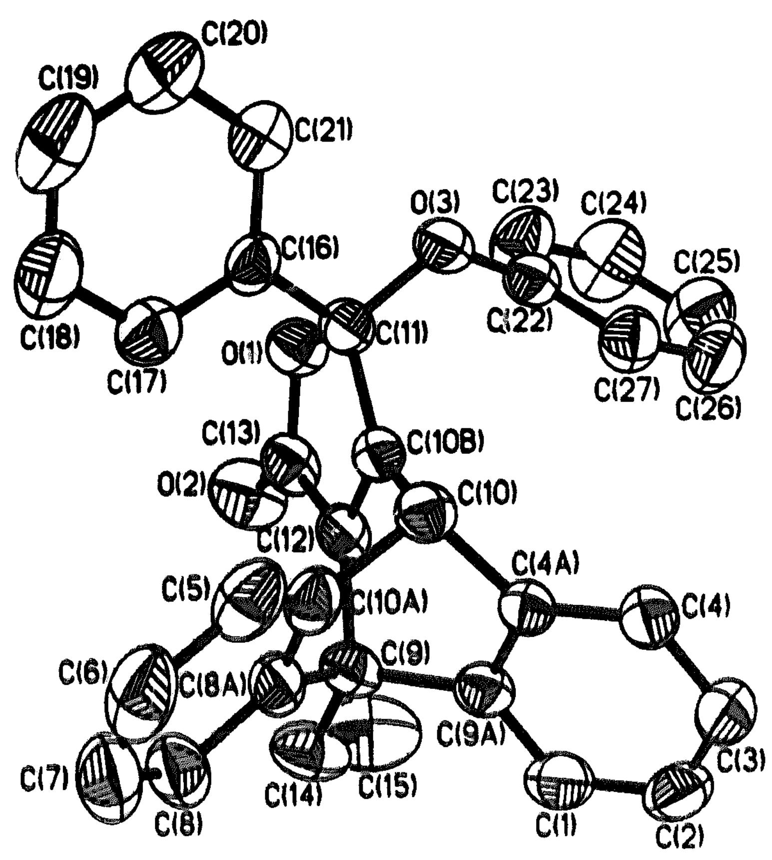


Fig. 3. Projection view of 20 with 50% probability ellipsoids.

to the diradical intermediate 2, which in turn can lead to the 8b-substituted dibenzosemibullvalene 6, whereas a [4a,11] bridging would give rise to the diradical intermediate 4, which in turn could lead to the 4b-substituted dibenzosemibullvalene 5. A dibenzosemibullvalene such as 6, bearing three substituents on the cyclopropane ring present in it, would be relatively unstable and could lead, through either a thermal or photochemical process, to the diradical intermediate 9. Oxygen quenching of 9 would give the endoperoxide 8, which could be the precursor of 12. It may be mentioned in this connection that Scheffer [9] and coworkers have isolated a peroxide, analogous to 8, from the photorearrangement of dimethyl-9,10-dichloro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate and confirmed its structure through X-ray crystallographic analysis. A cyclic peroxide, analogous to 8, has also been invoked as an intermediate in the photorearrangement of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene, leading to oxygenated products [3]. Subsequent photoexcitation of 8 could lead to a new diradical 7 which could undergo a radical cyclization to give 11. Air oxidation of 11 would result in the formation of 12, as shown in Scheme 1.

The formation of the lactonic product 20 from 1, on irradiation in the presence of oxygen, suggests that, besides the usually observed dibenzosemibullvalene rearrangement leading to dibenzocyclooctatetraenes and dibenzosemibullvalenes, the dibenzoylalkene type of rearrangement [10] is also taking place in this case. A reasonable pathway for the formation of 20 from 1 is shown in Scheme 2. Initial excitation of 1, followed by rapid intersystem crossing, would give its triplet state, which can subsequently lead to the diradical intermediate 13. It may be pointed out that the involvement of such diradical intermediates have been postulated in the photorearrangement of 1,2-dibenzoylalkenes [3]. The fact that we have not been able to isolate any ketene-derived product such as 17 from the photoreaction of 1 would suggest that in this case the diradical 13 may be being quenched by oxygen present to give a peroxy radical 16, which can ultimately lead to 20, as shown in Scheme 2.

It is interesting to note that in the photolysis of 1, bearing an ethyl group at the bridgehead position (C(9)), gives rise to both dibenzosemibullvalenes 5 and 6 (Scheme 1), whereas the photolysis of 9-methyl-substituted dibenzosemibullvalene is reported to give exclusively the 4b-methyl-substituted dibenzosemibullvalene, analogous to 5 [11]. It appears that, as the size of the C(9) substituent increases as in the case of 1, the tendency to relieve the steric interaction between the C(9) substituent and the hydrogen atoms at the C(1) and C(8) positions of the phenyl groups, through a pathway involving [9a,12] bridging and subsequent reorganization, increases. Similar observations have been made in the case of 9-aryl-substituted dibenzobarrelenes, in which the initially formed dibenzosemibullvalenes undergo a ring-enlargement reaction leading to dibenzofuranopentalenes [12].

Acknowledgements

We thank the Council of Scientific and Industrial Research, Government of India (T.M., S.A.K., S.D. and M.V.G.), National Science Foundation (CHE-9309690), Missouri Research Board, Center for Molecular Sciences and Department of Chemistry of the University of Missouri-St. Louis (N.P.R.) and the Office of Basic Energy Sciences of the US Department of Energy (M.V.G. (in part)) for financial support of this work.

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