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Substituent Effects on Regioselectivity in the Photorearrangement of a Few Naphthobarrelenes[1]

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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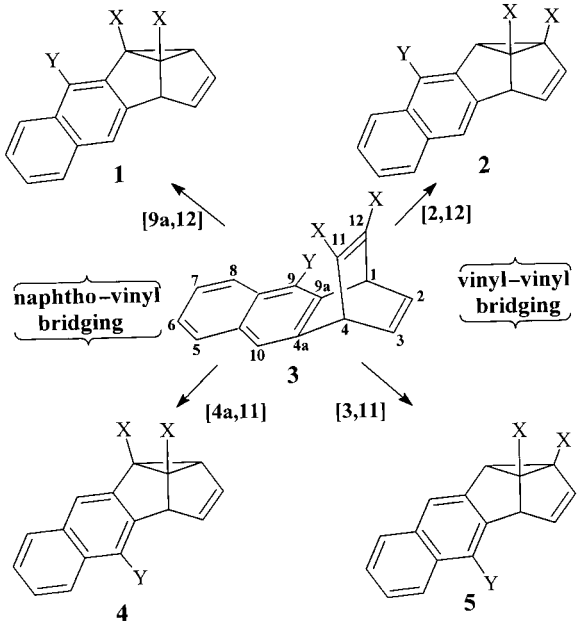
Abstract—The photorearrangement of a few 9,10-disubstituted-naphthobarrelenes to the corresponding naphthosemibullvalenes has been examined. It was observed that the regioselectivity in these photoisomerizations depends on the relative stabilities of the diradical intermediates. AM1 semi-empirical calculations are in support of this view. Thermal transformation of the naphthosemibullvalenes gave the corresponding water added naphthopentalenofurans, in nearly quantitative yields.

Introduction

The di-π-methane rearrangement of barrelenes,[2] benzobarrelenes,[3] dibenzobarrelenes[4] and naphthobarrelenes[5] has been extensively investigated. All these derivatives undergo photorearrangement to the corresponding semibullvalenes and/or cyclooctatetraenes depending upon the reaction conditions. The semibullvalenes are known to arise through a triplet state mediated pathway, whereas direct irradiation leads to the singlet state mediated cyclooctatetraene derivatives.[6] There has been considerable interest in recent years to understand the factors that are responsible for the observed regioselectivity in the photorearrangement of barrelenes, leading to semibullvalenes.

As in the case of substituted dibenzobarrelene derivatives, which yield two regioisomeric dibenzosemibullvalenes, on irradiation,[7] the corresponding naphthobarrelenes can, in principle, yield four regioisomers (Scheme 1). For example, a substituted naphthobarrelene such as **3** can undergo an initial naphtho–vinyl bridging leading to the formation of regioisomers **1** and **4**, whereas the initial vinyl–vinyl bridging can lead to the regioisomers **2** and **5**. It has been observed that, as in the case of benzobarrelenes[3] and 2,3-anthracenobarrelenes,[8] an initial vinyl–vinyl bonding is the preferred mode of bridging in the photorearrangement of 2,3-naphthobarrelenes.[5a,b] However, in the case of 1,2-naphthobarrelenes, the major pathway involves an initial naphtho–vinyl bridging.[5a,b] Although attempts have been made to rationalize these observations by deuterium-labeling studies of 1,2-naphthobarrelenes, the effects of substituents on the initial mode of bonding as well as the observed regioselectivity in the photorearrangement of 2,3-naphthobarrelenes have not so far been examined.



Scheme 1.

Keywords: di-π-methane rearrangement; naphthobarrelenes; naphthosemibullvalenes; regioselectivity.
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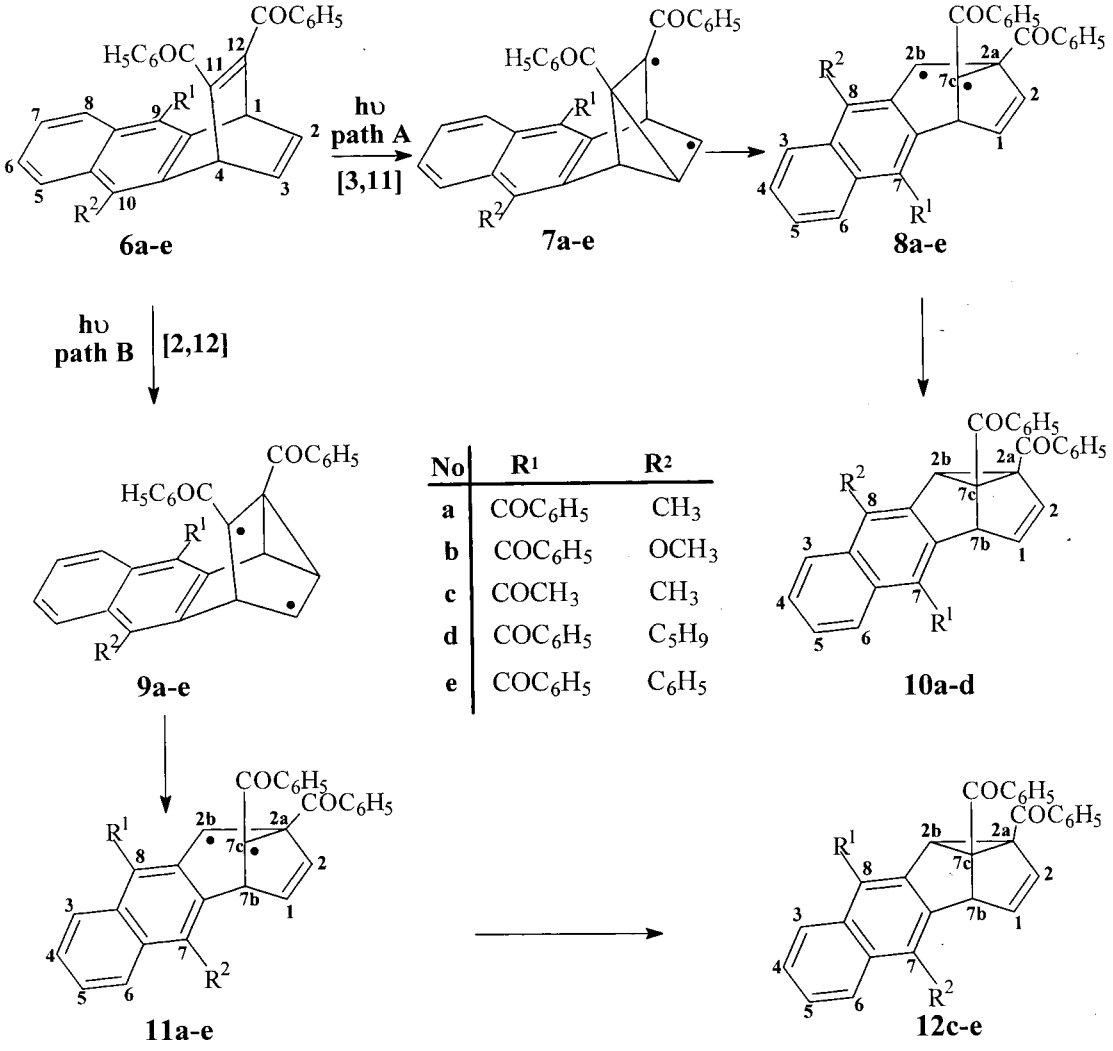
In the present investigation, we have examined the photorearrangement of a few disubstituted 2,3-naphthobarrelenes containing 1,2-dibenzoylalkene moieties (**6a–e**). These results indicate that in the rearrangement of naphthobarrelenes to the corresponding semibullvalenes, steric effects exerted by the substituents have a bearing on the observed regioselectivity. Another aspect of the present study deals with the thermal transformations of the naphthosemibullvalenes formed in these reactions. Interestingly, the thermal transformations of representative naphthosemibullvalenes **10a**, **10b** and **12e**, yielded the corresponding dihydropentalenofurans as the primary products, which underwent water addition during work-up, to yield the corresponding tetrahydropentalenofuran derivatives **14a**,**b**,**e**.

Results

Steady-state photolysis and product identification

The starting naphthobarrelenes **6a–e**, containing 1,2-dibenzoylalkene moieties were prepared through the reaction of the appropriate anthracenes with dibenzoylacetylene (DBA) by neat heating or in the presence of a Lewis acid catalyst such as aluminium chloride. The corresponding dibenzobarrelenes were also isolated under these conditions. The structures of the naphthobarrelenes **6a–e** have been arrived at on the basis of analytical results and spectral data. The ^{1}H NMR spectrum of **6a**, for example, showed the bridgehead protons at δ 5.18 and 5.87 as doublets. In the case of **6d**, the ^{13}C NMR spectrum showed five carbons corresponding to the cyclopentyl group over the range δ 27.76–40.00, indicating a restricted orientation for the cyclopentyl group.

Photolysis of **6a** in benzene gave the regiospecific naphthosemibullvalene **10a** in a 90% yield (Scheme 2). Yields reported herein are the isolated yields of products, after purification through recrystallization, unless otherwise stated. The ^{1}H NMR spectrum of **10a** showed the allylic bridgehead proton as a doublet at δ 4.42, while the proton attached to the cyclopropane ring appeared as a singlet at δ 4.82. The ^{13}C NMR spectrum of **10a** showed four bridgehead carbons over the range δ 48.08–71.69. The structure of **10a** was further confirmed through X-ray crystallographic analysis.[10]



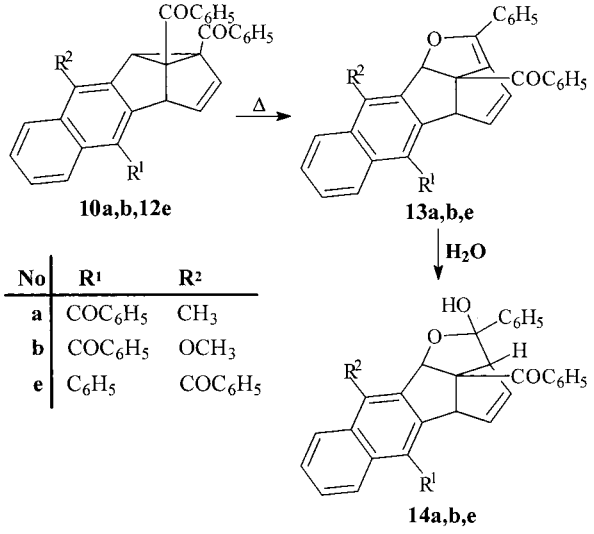
Scheme 2.

Table 1. Regioisomeric product distribution in the phototransformations of naphthobarrelenes **6a–e** (irradiated in benzene with RPR 300 nm light source and the yields are calculated on the basis of 100% product balance)

Entry	Disubstituted naphthobarrelene	**10** (%) path A	**12** (%) path B
1	**6a** (methyl, benzoyl)	100	0
2	**6b** (methoxy, benzoyl)	100	0
3	**6c** (acetyl, methyl)	47	53
4	**6d** (cyclopentyl, benzoyl)	35	65
5	**6e** (phenyl, benzoyl)	0	100

Irradiation of **6b**, similarly gave the regiospecific isomer **10b** in a 88% yield. The structure of **10b** was also confirmed through X-ray crystallographic analysis.[10] Interestingly, irradiation of 9-acetyl-10-methylnaphthobarrelene **6c**, under analogous conditions, yielded both the regioisomers **10c** (31%) and **12c** (35%), along with 20% of the unchanged starting material (Scheme 2). Yields of various regioisomers calculated on the basis of 100% product balance are summarized in Table 1 and were confirmed by ^{1}H NMR spectroscopy monitoring of these photoreactions. The structures of the regioisomers **10c** and **12c** were arrived at on the basis of spectral data and analytical evidence. The ^{1}H NMR spectrum of **10c** showed the allylic bridgehead proton as a doublet at δ 4.74, whereas it appeared as a doublet at δ 4.55 in its regioisomer **12c**, showing a net shielding effect of 0.19 ppm. Similarly, the cyclopropane ring proton of **10c** appeared as a singlet at δ 4.62, whereas it was observed at δ 4.75 in the case **12c**, indicating a net deshielding effect of 0.13 ppm.

Irradiation of 9-benzoyl-10-cyclopentylnaphthobarrelene **6d**, similarly, gave a mixture of regioisomers **10d** (23%) and **12d** (43%) in the ratio of 1:1.9. The spectral patterns of **10d** and **12d** closely resemble those of the regioisomers **10c** and **12c**. The allylic bridgehead proton of **10d** appeared as a doublet at δ 4.70, while it appeared as a doublet at δ 4.38 in the case of **12d** with a net shielding of 0.32 ppm. Similarly, the cyclopropane ring proton of **10d** appeared as a singlet at δ 4.67, whereas it was observed along with one of the vinylic protons at δ 5.28 in **12d**, showing a net deshielding effect of 0.62 ppm. Interestingly, irradiation of the 9-benzoyl-10-phenylnapthobarrelene **6e** gave the regiospecific isomer **12e** in a 58% yield, along with the unchanged starting material **6e** (30%). The structure of **12e** was confirmed through X-ray crystallographic analysis.[10]



Scheme 3.

Thermal transformations of naphthosemibullvalenes 10a, 10b and 12e

It has been observed earlier that dibenzosemibullvalenes containing dibenzoyl groups attached to the cyclopropane ring undergo interesting isomerization to the corresponding dibenzodihydropentalenofuran derivatives.[7,9] In order to examine the type of products formed in the case of naphthosemibullvalenes, a few representative examples were subjected to thermolysis. The thermal isomerization of **10a** in *o*-dichlorobenzene for 20 min gave a 82% of the corresponding water added tetrahydropentalenofuran derivative **14a**, after purification by column chromatography (Scheme 3). Similarly, the thermolysis of **10b** and **12e**, under analogous conditions, gave the water added tetrahydropentalenofuran derivatives **14b** and **14e** in 72% and 60% yields, respectively. The ^{1}H NMR spectrum of **14a**, for example showed the tertiary hydroxyl proton at δ 3.09, as a singlet. The two allylic bridgehead protons were observed at δ 4.63 and 4.94, whereas the vinylic protons appeared at δ 4.94 and 5.88, respectively as multiplets. The ^{13}C NMR spectrum of **14a** showed the hemiacetal carbon at δ 108.55, whereas the benzylic carbon, substituted with the ether linkage was observed at δ 85.10. The structure of **14a** was also confirmed through DEPT-135 NMR technique. Compounds **14b** and **14e** also displayed similar spectral features. As a representative example, the structure of **14b** was further confirmed through X-ray crystallographic analysis.[10]

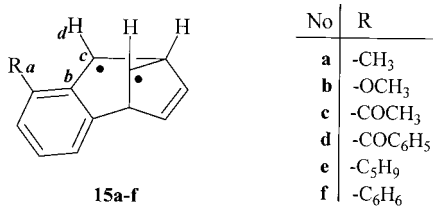
In order to confirm the formation of naphthopentalenofurans **13a**, **13b** and **13e** as primary products in these reactions, control experiments were carried out in NMR tubes under dry conditions. For example, compound **10a** was subjected to neat thermolysis at 180°C for 2 min in a NMR tube in an oil bath. The solvent $CDCl_3$ was added afterwards and recorded the ^{1}H and ^{13}C NMR spectra. Spectral analysis showed the formation of the corresponding dihydropentalenofuran derivative **13a** as the exclusive product. The ^{1}H NMR spectrum showed the allylic bridgehead proton at δ 4.63 whereas the adjacent vinylic proton appeared as a multiplet at δ 5.80. The other vinylic proton appeared as a doublet at δ 6.46, while the benzylic proton of the pentalenofuran ring was observed at δ 6.43 as a singlet. The ^{13}C NMR spectrum showed the carbonyl carbons at δ 198.68 and 199.77. In a separate experiment, when **10b** was thermolyzed and analyzed as in the case of **10a**, it showed the formation of the corresponding dihydropentalenofuran derivative **13b** as the exclusive primary product.

Discussion

The mechanism for the formation of regioisomeric products **10** and **12** in the phototransformations of naphthobarrelenes **6a–e** can be rationalized in terms of the pathways shown in

Table 2. The torsional angles associated with the diradical intermediates **15a–f**, generated by AM1 semi-empirical molecular orbital calculations (subject to constraints, for the maximum steric effects by the substituents on the radical center)

Entry	Torsional angle, *abcd* (°)
15a	0.49
15b	0.40
15c	0.59
15d	0.94
15e	9.68
15f	12.17



15a-f

No	R
a	$-CH_3$
b	$-OCH_3$
c	$-COCH_3$
d	$-COC_6H_5$
e	$-C_5H_9$
f	$-C_6H_6$

Chart 1.

Scheme 2. As mentioned earlier, 2,3-naphthobarrelenes **6a–e**, containing 1,2-dibenzoylalkene moieties, undergo photoisomerization, channeled exclusively through an initial vinyl–vinyl bonding. This bonding can proceed either through a [3,11] bridging (path A) or [2,12] bridging (path B) leading to the primary diradical intermediates **7** and **9**, respectively. These diradicals can subsequently undergo transformation to the corresponding secondary diradical intermediates **8** and **11** and leading ultimately to the regioisomeric naphthosemibullvalenes **10** and **12**, respectively. The observed regioselectivity in these cases may be dependent on the stabilities of the primary (**7** and **9**) and secondary (**8** and **11**) diradical intermediates, respectively. In the case of the primary diradicals **7** and **9**, the effects of the substituents are not expected to be significant since the substituents are far removed from the radical site. Therefore, the observed regioselectivity in these reactions may be directly related to the stabilities of the secondary 1,3-diradical intermediates **8** and **11**, wherein one can anticipate significant steric effects of the substituents.

If we consider the diradical intermediate **11a** derived from **6a**, for example, one can expect some amount of steric interference between the bulky benzoyl substituent at the C-8 position and the hydrogen atom at the radical center at **2b** position. The consequence of this will be a distortion in the planarity of the radical center, thereby resulting in a net destabilization of the diradical intermediate **11a**[11,12] (i.e. the extent of delocalization of the free electron in the p orbital of the sp^2 hybridized carbon atom with the naphthalene moiety is decreased due to the distortion in planarity). In the case of diradical intermediate **8a**, however, such steric effects are minimal as the methyl group at the C-8 position is well separated from the radical center. Therefore, the reaction of **6a** is channeled through path 'a' involving the stable diradical intermediate **8a**. A similar rationalization holds good for the formation of **10b** from **6b**.

In order to have a qualitative picture of the steric effects exerted by the substituents, AM1 semi-empirical molecular orbital calculations[13] were carried out for the model diradical intermediates **15a–f** (Table 2, Chart 1). These calculations were performed, subject to constraints, for the maximum steric effects by the substituents on the hydrogen atom of the radical center. A quantitative account of the extent of distortion in planarity of the radical center can be obtained from the torsional angle *abcd*. It was found that, as the bulkiness of the substituent increases the torsional angle also increases, thereby indicating a net distortion in planarity. For example, the model diradical intermediate **15a** (corresponding **8a**), where the methyl group is *syn* to the radical center exhibited a dihedral angle of 0.49°, whereas the model diradical intermediate **15d** (corresponding **11a**) showed a dihedral angle of 0.94°, indicating a higher extent of destabilization in the latter case.

Interestingly, in the case of **6c**, where both the regioisomers (**10c** and **12c**) are formed in nearly equal amounts, both the pathways are equally favored. In contrast, in the case of **6d**, the product (**12d**) arising through path B was found to be nearly double that of the product (**10d**) arising through path A. This again supports the view that with increase in the bulkiness of the substituent (cyclopentyl) the diradical intermediate **8** is destabilized, thereby favoring a pathway mediated through the diradical intermediate **11**. The AM1 calculations for the respective model diradical **15e**, showed a torsional angle of 9.68°, in support of this view. Electronic effects such as electron withdrawing ability of the C-9 substituent in controlling the regioselectivity can be ruled out in these cases since the photoproduct distribution in **6a–d** are significantly different. Additional support for the role of steric effects in controlling regioselectivity was derived through the photorearrangement of the naphthobarrelene **6e**, having benzoyl and phenyl groups at 9 and 10 positions, respectively. Depending on the excited state orientation, the phenyl group can exert effective steric interference (torsional angle 12.17°) through the perihydrogens[14] (Chart 1, **15f**). It is therefore not surprising to note that the photoisomerization of **6e** gave exclusively the regioisomer **12e**, channeled through path B.

The thermal isomerization of naphthosemibullvalenes **10a**, **10b** and **12e** is analogues to that of the dibenzosemibullvalenes which are reported to give dihydropentalenofuran derivatives.[7,9] However, the naphthodihydropentalenofurans formed in the thermolysis of the corresponding semibullvalenes were found to readily add a molecule of water, under the conditions of work-up, yielding the water-added products. It is interesting to note that a 1,2 addition of water is the preferred mode and that the ease of addition may reflect the release of strain in going from **13a**,**b**,**e** to the corresponding water added products **14a**,**b**,**e**.

Conclusions

The observed regioselectivity in the photoisomerization of naphthobarrelenes **6a–e** can be rationalized in terms of the relative stabilities of the diradical intermediates (**8a–e** and **11a–e**) derived from the initially formed primary diradical intermediates (**7a–e** and **9a–e**). It was observed that steric effects of the nearby substituents to the radical centre play a

dominant role with respect to the stabilities of **8a–e** and **11a–e**. AM1 semi-empirical calculations of the respective model diradicals support this view. Thermal isomerization of representative naphthosemibullvalenes **10a**, **10b** and **12e** led to the corresponding naphthodihydropentalenofurans **13a**,**b**,**e** in nearly quantitative yields.

Experimental

The equipment and procedure for melting point determination and spectral recordings are described in earlier publications.[15] All steady-state irradiation experiments were carried out in a Srinivasan–Griffin–Rayonet Photochemical Reactor (RPR 300 nm) or by using a Pyrex filtered light from a Hanovia 450 W medium pressure mercury lamp, under inert conditions. Solvents for photolysis experiments were purified and distilled before use. Petroleum ether used was the fraction with a bp 60–80°C.

Starting materials

Dibenzoylacetylene (DBA),[16] mp 110–111°C; 9-benzoyl-10-methylanthracene,[17] mp 175–176°C, 9-benzoyl-10-methyoxyanthracene,[18] mp 174–175°C, 9-acetyl-10-methylanthracene,[19] mp 135–136°C; 9-benzoyl-10-cyclopentylanthracene,[19] mp 135–136°C and 9-benzoyl-10-phenylanthracene,[20] mp 174–175°C were prepared by reported procedures.

Preparation of the naphthobarrelene derivatives 6a–e

The naphthobarrelenes were prepared through the Diels–Alder reaction of the appropriate anthracene derivatives with DBA under neat heating or in the presence of anhydrous aluminium chloride. Small amounts of the corresponding dibenzobarrelenes were also isolated, in each case, under these conditions.

9-Benzoyl-10-methylnaphthobarrelene (6a). To a mixture of 9-benzoyl-10-methylanthracene (0.74 g, 2.5 mmol) and $AlCl_3$ (310 mg, 2.5 mmol) in dichloromethane (20 mL) was added DBA (0.58 g, 2.5 mmol) in dichloromethane (20 mL) and stirred for 1 h at room temperature. The reaction mixture was acidified with hydrochloric acid (6.5 N, 200 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 148 mg (20%) of the unchanged anthracene derivative, mp 176–177°C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 157 mg (12%) of the corresponding dibenzobarrelene derivative, mp 226–227°C (mixture mp), followed by 750 mg (57%) of **6a**, mp 203–204°C: IR ν_{max} (KBr) 1668 cm^{-1}; UV λ_{max} (CH_3CN) 238 nm (ϵ 73,800); ^1H NMR ($CDCl_3$) δ 2.90 (3H, s), 5.18 (1H, d, J=5.4 Hz), 5.87 (H, d, J=5.4 Hz), 7.00–8.10 (21H, m); ^{13}C NMR ($CDCl_3$) δ 14.52, 48.22, 49.02, 128.21, 128.42, 128.47, 129.74, 138.74, 138.82, 152.23, 152.89, 193.27, 194.60, 198.35; exact mol wt calcd for $C_{38}H_{26}O_3$: 530.1882. Found: 530.1876 (high-resolution mass spectrometry). Anal. Calcd for $C_{38}H_{26}O_3$: C, 86.04; H, 4.90. Found: C, 85.93; H, 5.00.

9-Benzoyl-10-methoxynaphthobarrelene (6b). Reaction of 9-benzoyl-10-methoxyanthracene (1.56 g, 5 mmol) with DBA (1.17 g, 5 mmol) in the presence of $AlCl_3$ (0.67 g, 5 mmol) in dichloromethane (40 mL) and work-up as in the earlier case gave 624 mg (40%) of the unchanged starting anthracene derivative, mp 174–175°C (mixture mp), followed by 625 mg (20%) of the dibenzobarrelene derivative, mp 246–247°C (mixture mp) and 950 mg (35%) of **6b**, mp 187–188°C, after recrystallization from cyclohexane: IR ν_{max} (KBr) 1666 cm^{-1}; UV λ_{max} (CH_3CN) 240 nm (ϵ 76,700); ^1H NMR ($CDCl_3$) δ 4.18 (3H, s), 5.21 (1H, d, J=5.7 Hz), 5.95 (1H, d, J=5.8 Hz), 7.02–8.19 (21H, m); ^{13}C NMR ($CDCl_3$) δ 45.57, 48.89, 63.13, 122.36, 128.14, 128.27, 128.42, 129.75, 133.80, 139.08, 150.84, 152.09, 152.88, 193.08, 194.59, 197.76; exact mol wt calcd for $C_{38}H_{26}O_4$: 546.1831. Found: 546.1820 (high-resolution mass spectrometry). Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.52; H, 4.76. Found: C, 83.28; H, 4.84.

9-Acetyl-10-methylnaphthobarrelene (6c). A mixture of 9-acetyl-10-methylanthracene (1 g, 5 mmol) and DBA (1 g, 5 mmol) was well powdered and heated in an oil bath at 180–200°C for 20 min. The crude reaction mixture was recrystallized from a mixture (1:4) of methanol and dichloromethane to give 800 mg (40%) of the corresponding dibenzobarralene derivative, mp 226–227°C (mixture mp). The mother liquor was chromatographed over silica gel. Elution with a mixture (1:4) of ethyl acetate and hexane gave 400 mg (40%) of the unchanged anthracene derivative mp 136–137°C (mixture mp). Further elution gave 150 mg (8%) of **6c**, mp 209–210°C, after recrystallization from a mixture (4:1) of dichloromethane and methanol: IR ν_{max} (KBr) 1730, 1667 cm^{-1}; UV λ_{max} (CH_3CN) 251 nm (ϵ 72,300); ^1H NMR ($CDCl_3$) δ 2.73 (3H, s), 2.76 (3H, s), 5.46 (1H, d, J=4.2 Hz), 5.85 (1H, d, J=4.2 Hz), 7.09–8.04 (16H, m); ^{13}C NMR ($CDCl_3$) δ 14.50, 33.63, 48.00, 48.73, 124.86, 125.05, 126.37, 126.51, 126.74, 128.32, 128.44, 128.56, 130.58, 132.92, 132.96, 133.27, 136.23, 137.66, 137.73, 138.23, 138.31, 139.12, 152.36, 152.56, 194.31, 194.42, 206.57; exact mol wt calcd for $C_{33}H_{24}O_3$: 469.1804. Found: 469.1820 (high-resolution mass spectrometry). Anal. Calcd for $C_{33}H_{24}O_3$: C, 84.61; H, 5.13. Found: C, 84.92; H, 5.00.

9-Benzoyl-10-cyclopentylnaphthobarrelene (6d). A well powdered mixture of 9-benzoyl-10-cyclopentyl-anthracene (700 mg, 2 mmol) and DBA (600 mg, 2.5 mmol) was heated in an oil bath at 180–200°C for 90 min. The solid residue was chromatographed over silica gel. Elution with a mixture (1:4) of ethyl acetate and hexane gave 200 mg (28%) of the unchanged anthracene derivative, mp 173–174°C (mixture mp) followed by 150 mg (15%) of the adduct **6d**, mp 231–232°C, after recrystallization from a mixture (1:1) of dichloromethane and methanol: IR ν_{max} (KBr) 1681 cm^{-1}; UV λ_{max} (CH_3CN) 258 nm (ϵ 73,100); ^1H NMR ($CDCl_3$) δ 1.90–2.13 (8H, m), 4.23 (1H, m), 5.19 (1H, d, J=5.6 Hz), 5.98 (1H, d, J=5.2 Hz), 7.05–8.22 (21H, m); ^{13}C NMR (C_6D_6) δ 27.76, 27.87, 33.65, 33.98, 40.00, 48.99, 49.68, 125.13, 126.07, 127.10, 127.70, 128.34, 128.91, 129.77, 130.06, 132.65, 133.53, 138.82, 152.29, 152.66, 192.99, 194.60, 198.03. Anal. Calcd for $C_{42}H_{32}O_3$: C, 86.30; H, 5.48. Found: C, 86.60; H, 5.72.

9-Benzoyl-10-phenylnaphthobarrelene (6e). To a mixture of 9-benzoyl-10-phenylanthracene (1.79 g, 5 mmol) and anhydrous $AlCl_3$ (0.7 g, 5 mmol) in dichloromethane (30 mL) was added a solution of DBA (1.17 g, 5 mmol) in dichloromethane (20 mL). The mixture was stirred for 1.5 h at room temperature, acidified with hydrochloric acid (6.5 N, 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 800 mg (44%) of the unchanged anthracene derivative, mp 218–219°C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 600 mg (40%) of **6e**, mp 213–214°C: IR ν_{max} (KBr) 1664, 1652 cm^{-1}; UV λ_{max} (CH_3CN) 241 nm (ϵ 73,300); ^1H NMR ($CDCl_3$) δ 5.3 (2H, m), 7.01–7.98 (26H, m); ^{13}C NMR ($CDCl_3$) δ 48.63, 49.05, 125.33, 126.20, 126.44, 126.85, 127.66, 127.99, 128.08, 128.23, 128.35, 128.56, 128.64, 129.66, 130.11, 130.43, 131.09, 132.52, 133.77, 135.15, 136.97, 137.21, 138.31, 138.94, 151.08, 153.56, 192.79, 194.46, 198.01; mass spectrum *m/e* (relative intensity) 592 (M^+, 21), 487 (16), 105(100). Anal. Calcd for $C_{43}H_{28}O_3$: C, 87.16; H, 4.73. Found: C, 87.38; H, 4.77.

Photolysis of 6a. A solution of **6a** (500 mg, 0.9 mmol) in benzene (300 mL) was irradiated (Hanovia 450 W) for 60 min and removal of the solvent under vaccum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:4) of ethyl acetate and hexane gave 450 mg (90%) of **10a**, mp 180–181°C, after recrystallization from acetonitrile: IR ν_{max} (KBr) 1670 cm^{-1}; UV λ_{max} (CH_3CN) 239 nm (ϵ 74,900); ^1H NMR ($CDCl_3$) δ 2.90 (3H, s), 4.42 (1H, d, *J*=2.4 Hz), 4.82 (1H, s), 5.57 (1H, d, *J*=5.3 Hz), 6.01 (1H, m), 7.25–7.96 (19H, m); ^{13}C NMR ($CDCl_3$) δ 16.13, 48.08, 57.88, 65.09, 71.69, 123.02, 128.36, 128.48, 128.72, 129.93, 136.59, 145.33, 195.10, 197.84; exact mol wt calcd for $C_{38}H_{26}O_3$: 530.1882. Found: 530.1871 (high-resolution mass spectrometry). Anal. Calcd for $C_{38}H_{26}O_3$: C, 86.04; H, 4.90. Found: C, 85.76; H, 4.87.

Photolysis of 6b. A benzene solution (100 mL) of **6b** (200 mg, 0.4 mmol) was irradiated using RPR 300 nm for 60 min and work-up of the reaction mixture as in the earlier case gave 176 mg (88%) of **10b**, mp 183–184°C, after recrystallization from acetonitrile: IR ν_{max} (KBr) 1668 cm^{-1}; UV λ_{max} (CH_3CN) 245 nm (ϵ 45,600); ^1H NMR (C_6D_6) δ 3.91 (3H, s), 4.41 (1H, d, *J*=2.3 Hz), 5.21 (1H, s), 5.23 (1H, d, *J*=5.3 Hz), 5.94 (1H, m), 6.87–8.12 (19H, m); ^{13}C NMR (C_6D_6) δ 48.11, 57.93, 60.93, 64.32, 74.98, 120.28, 123.10, 123.89, 125.64, 126.01, 127.22, 127.70, 128.34, 128.61, 128.90, 130.06, 130.18, 132.58, 132.79, 133.46, 136.41, 137.11, 138.72, 149.44, 156.48, 194.50, 196.96; exact mol wt calcd for $C_{38}H_{26}O_4$: 546.1831. Found: 546.1830 (high-resolution mass spectrometry). Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.52; H, 4.76. Found: C, 83.27; H, 4.95.

Photolysis of 6c. A solution of **6c** (150 mg, 0.23 mmol) in benzene (50 mL) was irradiated using RPR 300 nm for 90 min. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel using a chromatotron. Elution with a mixture (1:9) of ethyl acetate and hexane gave 55 mg (35%) of **12c**, mp 198–199°C, after recrystallization from a mixture (1:1) of dichloromethane and methanol: IR ν_{max} (KBr) 1731, 1657 cm^{-1}; UV λ_{max} (CH_3CN) 239 nm (ϵ 71,700); ^1H NMR ($CDCl_3$) δ 2.65 (3H, s), 2.85 (3H, s), 4.55 (1H, d, *J*=2.1 Hz), 4.75 (1H, s), 5.58 (1H, d, *J*=5.1 Hz), 6.06 (1H, m), 7.08–8.11 (14H, m); ^{13}C NMR ($CDCl_3$) δ 16.17, 32.77, 47.95, 58.21, 65.37, 71.17, 123.05, 124.56, 125.06, 125.87, 126.32, 126.52, 128.28, 128.45, 128.61, 128.81, 129.31, 132.46, 132.99, 133.25, 133.63, 134.60, 136.01, 136.68, 143.92, 195.00, 195.27, 204.75; exact mol wt calcd for $C_{33}H_{24}O_3$: 468.1725. Found: 468.1728 (high-resolution mass spectrometry). Anal. Calcd for $C_{33}H_{24}O_3$: C, 84.61; H, 5.13. Found: C, 84.49; H, 5.01.

Further elution gave 30 mg (20%) of the unchanged starting naphthobarrelene **6c**, mp 209–210°C (mixture mp), followed by 45 mg (31%) of **10c**, mp 189–190°C, after recrystallization from a mixture (1:1) of dichloromethane and methanol: IR ν_{max} (KBr) 1732, 1654 cm^{-1}; UV λ_{max} (CH_3CN) 243 nm (ϵ 71,200); ^1H NMR ($CDCl_3$) δ 2.65 (3H, s), 2.77 (3H, s), 4.62 (1H, s), 4.74 (1H, d, *J*=2.2 Hz), 5.59 (1H, d, *J*=5.2 Hz), 5.99 (1H, m), 7.39–8.02 (16H, m); ^{13}C NMR ($CDCl_3$) δ 14.99, 32.77, 48.42, 57.09, 65.37, 71.73, 123.16, 124.19, 125.28, 126.24, 126.32, 128.19, 128.42, 128.62, 128.74, 129.11, 129.56, 132.01, 132.04, 133.07, 133.18, 134.78, 136.53, 145.67, 194.81, 195.18, 204.62; exact mol wt calcd for $C_{33}H_{24}O_3$: 468.1725. Found: 468.1740 (high-resolution mass spectrometry). Anal. Calcd for $C_{33}H_{24}O_3$: C, 84.61; H, 5.13. Found: C, 84.38; H, 5.11.

Photolysis of 6d. A solution of **6d** (150 mg, 0.20 mmol) in benzene (50 mL) was irradiated using RPR 300 nm for 60 min. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel using a chromatotron. Elution with a mixture (1:9) of ethyl acetate and petroleum ether gave (65 mg, 43%) of **12d**, mp 211–212°C, after recrystallization from a mixture (1:1) of dichloromethane and methanol: IR ν_{max} (KBr) 1664 cm^{-1}; UV λ_{max} (CH_3CN) 265 nm (ϵ 72,900); ^1H NMR (C_6D_6) δ 1.92–2.48 (8H, m), 3.93 (1H, m), 4.38 (1H, d, *J*=1.7 Hz), 5.28 (2H, s), 5.88 (1H, m), 6.81–8.13 (19H, m); ^{13}C NMR (C_6D_6) δ 27.17, 27.64, 32.05, 34.64, 41.30, 50.00, 57.43, 64.27, 75.04, 123.82, 124.72, 125.68, 126.19, 127.70, 128.34, 128.93, 129.43, 130.06, 131.42, 132.51, 133.60, 136.47, 138.17, 143.15, 146.76, 194.51, 194.90, 197.61. Anal. Calcd for $C_{42}H_{32}O_3$: C, 86.30; H, 5.48. Found: C, 86.60; H, 5.49.

Further elution gave a mixture of **6d** and **10d**, which were separated by fractional recrystallization from a mixture (2:1) of dichloromethane and acetonitrile to give 30 mg (20%) of **6d**, mp 231–232°C (mixture mp) and 35 mg (23%) of **10d**, mp 203–204°C: IR ν_{max} (KBr) 1667 cm^{-1}; UV λ_{max} (CH_3CN) 261 nm (ϵ 70,700); ^1H NMR (C_6D_6) δ 2.21–2.91 (8H, m), 3.40 (1H, m), 4.67 (1H, s), 4.70 (1H, d, *J*=1.5 Hz), 5.32 (1H, d, *J*=5.1 Hz), 5.62 (1H, m), 6.64–7.91 (19H, m); ^{13}C NMR (C_6D_6) δ 27.74, 27.85, 33.64, 33.98, 42.53, 48.77, 58.25, 65.13, 71.48, 123.17, 127.69, 128.33, 128.90, 133.54, 138.81, 139.55, 146.74, 152.31, 152.66, 194.21, 194.59, 198.04. Anal. Calcd for $C_{42}H_{32}O_3$: C, 86.30; H, 5.48. Found: C, 86.25; H, 5.38.

Photolysis of 6e. A benzene solution (300 mL) of **6e** (590 mg, 1 mmol) was irradiated (Hanovia 450 W) for 90 min. Removal of the solvent under vaccum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and petroleum ether gave (342 mg, 58%) of **12e**, mp 209–210°C, after recrystallization from a mixture (1:1) of chloroform and methanol: IR ν_{max} (KBr) 3056, 1686, 1680 cm^{-1}; UV λ_{max} (CH_3CN) 241 nm (ϵ 66,600); ^1H NMR ($CDCl_3$) δ 4.38 (2H, m), 5.52 (1H, d, J=5.2 Hz), 5.78 (1H, m), 7.25–7.74 (24H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.55, 57.53, 64.95, 71.84, 122.79, 126.37, 128.57, 128.82, 128.87, 135.81, 137.75, 145.65, 194.75, 194.96, 197.79. mass spectrum *m/e* (relative intensity) 592 (M^+, 20), 487 (14), 105 (100). Anal. Calcd for $C_{43}H_{28}O_3$: C, 87.16; H, 4.73. Found: C, 86.93; H, 5.00.

Further elution gave 177 mg (30%) of the unchanged naphthobarrelene derivative **6e**, mp 213–214°C (mixture mp).

^1H NMR monitoring of the photoreactions of 6a–e

Solutions of **6a**–**e** (10–20 mg) in $CDCl_3$ or C_6D_6 (0.5 mL) in NMR tubes were irradiated with RPR 300 nm light source for ~30 min and analyzed the product mixture by ^1H NMR (300 MHz). The ^1H NMR spectrum, in each case, confirmed the ratios of photoproducts as reported earlier under the section dealing with steady-state photolysis, and thereby ruling out the possible formation of any other products in these phototransformations.

Thermal transformations of 10a, 10b and 12e

Thermal transformations of representative naphthosemibullvalenes **10a**, **10b** and **12e** (0.2 mmol) to the corresponding water added naphthopentaleneofurans **14a**, **14b** and **14e** were achieved by refluxing in *o*-dichlorobenzene (20 mL) for 20 min. The solvent was removed under vacuum and the residual solid thus obtained was chromatographed over silica gel using a chromatotron. Elution with a mixture (1:5) of ethyl acetate and hexane and recrystallization from a mixture (1:1) of acetonitrile and dichloromethane gave the desired product.

14a (82%), mp 239–240°C: IR ν_{max} (KBr) 1665 cm^{-1}; UV λ_{max} (CH_3OH) 249 nm (ϵ 64,500); ^1H NMR ($CDCl_3$) δ 2.93 (3H, s), 3.09 (1H, s, D_2O exchangeable), 4.06 (1H, s), 4.63 (1H, s), 4.94 (1H, m), 5.88 (1H, m), 6.69 (1H, s), 7.25–8.15 (19H, m); ^{13}C NMR ($CDCl_3$) δ 14.88, 61.29, 67.15, 72.37, 85.10, 108.55, 128.28, 127.43, 127.58, 127.73, 132.72, 136.79, 140.40, 197.56, 199.23; ^{13}C NMR (DEPT-135, $CDCl_3$) δ 14.00, 61.39, 66.29, 84.17, 124.37, 126.11, 126.54, 126.69, 126.84, 127.65, 128.01, 131.23, 131.84, 133.84. Anal. Calcd for $C_{38}H_{28}O_4$: C, 83.21; H, 5.11. Found: C, 83.48; H, 5.45.

14b (72%), mp 246–247°C: IR ν_{max} (KBr) 1661 cm^{-1}; UV λ_{max} (CH_3OH) 251 nm (ϵ 69,500); ^1H NMR ($CDCl_3$) δ 3.05 (1H, s, D_2O exchangeable), 3.98 (1H, s), 4.31 (3H, s), 4.54 (1H, s), 4.86 (1H, m), 5.82 (1H, m), 6.76 (1H, s), 7.16–8.26 (19H, m); ^{13}C NMR ($CDCl_3$) δ 60.97, 62.89, 73.84, 83.60, 85.73, 109.35, 122.07, 127.30, 127.56, 129.59, 129.70, 135.27, 137.86, 144.25, 155.37, 198.20, 199.80; exact mol wt calcd for $C_{38}H_{28}O_5$: 564.1937. Found 564.1941. (high-resolution mass spectrometry). Anal. Calcd for $C_{38}H_{28}O_5$: C, 80.45; H, 4.96. Found: C, 80.51; H, 4.86.

14e (60%), mp 218–219°C : IR ν_{max} (KBr) 1667 cm^{-1}; UV λ_{max} (CH_3OH) 257 nm (ϵ 74,300); ^1H NMR ($CDCl_3$) δ 3.96 (1H, s, D_2O exchangeable), 4.16 (1H, m), 4.59 (3H, s), 4.90 (1H, m), 5.84 (1H, m), 6.16 (1H, s), 7.19–7.84 (19H, m); ^{13}C NMR ($CDCl_3$) δ 62.32, 68.14, 73.85, 85.11, 108.98, 125.63, 125.86, 126.26, 126.66, 127.34, 127.74, 128.00, 128.35, 128.55, 128.83, 129.98, 130.80, 131.54, 132.08, 133.03, 133.90, 135.33, 140.32, 198.61, 199.64; ^{13}C NMR (DEPT-135, $CDCl_3$) δ 62.36, 68.00, 85.81, 125.67, 126.30, 126.71, 128.05, 128.41, 128.60, 128.89, 130.02, 131.58, 133.14135.40. Anal. Calcd for $C_{43}H_{30}O_4$: C, 84.59; H, 4.92. Found: C, 84.96; H, 5.25.

NMR monitoring of the thermal transformations of 10a and 10b

Thermal transformations of representative naphthosemibullvalenes **10a** and **10b** (20 mg) to the corresponding naphthopentalenofurans **13a** and **13b** were achieved by carrying out the neat thermolysis in NMR tubes in an oil bath maintained at 180°C for 2 min. $CDCl_3$ (0.5 mL) was immediately added to the thermolyzed mixtures and recorded both the ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C NMR spectra revealed the formation of only the corresponding naphthopentalenofurans in these reactions.

13a. ^1H NMR ($CDCl_3$) δ 2.99 (3H, s), 4.63 (1H, s), 5.80 (1H, m), 6.43 (1H, s), 6.46 (1H, d, J=5.4 Hz), 7.28–7.89 (19H, m); ^{13}C NMR ($CDCl_3$) δ 15.00, 55.60, 78.01, 87.85, 122.85, 126.62, 128.00, 128.70, 128.87, 133.01, 137.21, 148.38, 198.68, 199.77.

13b. ^1H NMR ($CDCl_3$) δ 4.38 (3H, s), 4.62 (1H, s), 5.82 (1H, m), 6.48 (1H, d, J=5.2 Hz), 6.60 (1H, s), 7.25–8.31 (19H, m); ^{13}C NMR ($CDCl_3$) δ 52.39, 61.30, 77.47, 85.51, 121.96, 125.40, 127.54, 127.66, 127.86, 132.89, 135.91, 146.73, 155.33, 197.30, 198.51.

X-Ray structure determination of 10a, 10b, 12e and 14b

Good quality crystals of **10a**, **10b**, **12e** and **14b** were mounted on glass fibers in random orientations and subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four circle diffractometer. Data reduction and structure solution were achieved by SHELXTL-PLUS (VMS) structure solution package.[10a] Details of the X-ray structures may be found at the Cambridge Crystallographic Data Center.[10b]

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