Biradical Intermediates in the Photoisomerization of Dibenzodihydropentalenofurans to Dibenzosemibullvalenes¹

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The photoisomerization of a few substituted dibenzodihydropentalenofurans to the corresponding dibenzosemibullvalenes is reported. Steady-state photolysis of the dibenzodihydropentalenofurans 3a-d gave the corresponding dibenzosemibullvalenes 2a-d in nearly quantitative yields. The quantum yields of this photoisomerization were found to be in the range 0.17–0.26. Laser flash photolysis studies of the dibenzodihydropentalenofurans 3a-e showed transients, with absorption maxima around 410 nm and decaying by first-order kinetics. The lifetimes were in the range 14-30 µs in degassed benzene at 25 °C. These transients were readily quenched (trapped) by molecular oxygen, and the Stern–Völmer quenching constants were found to be in the range (2.45–3.17) \times 10^9 M⁻¹ s⁻¹. As a representative example, the 1,3-biradical intermediate from **3e** was trapped by molecular oxygen to give the corresponding endoperoxide 11e. The transients were weakly quenched by triplet/radical quenchers such as 2,2,6,6-tetramethylpiperinyl-1-oxy (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperinyl-1-oxy (HTEMPO), and the quenching constants are found to be in the range $(1.09-3.19) \times 10^6$ M⁻¹ s⁻¹. The decay rates of the transients were found to be temperature dependent and obeyed the Arrhenius equation. For example, the activation energy of the transient from **3a** was \sim 4.5 kcal mol⁻¹ and the Arrhenius preexponential factor log(A/s⁻¹) for the decay of the transients was \sim 7.5. On the basis of our studies, these transients were assigned as the groundstate triplet biradicals, generated by the cleavage of the C-O bond of the starting dibenzodihydropentalenofurans.

Introduction

Several aspects of the phototransformations of dibenzobarrelenes are reported in the literature.³ Depending on the reaction conditions and the substituents, dibenzobarrelenes undergo photorearrangement, leading primarily to the corresponding dibenzosemibullvalenes and/or dibenzocyclooctatetraenes. It has been suggested that the dibenzocyclooctatetraenes are formed through a singletstate pathway, whereas the dibenzosemibullvalenes arise through triplet state mediated pathways. Recently, we had reported^{4a,b} the photoisomerization of a few dibenzobarrelene derivatives, containing dibenzoylalkene moiety

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(Scheme 1). Thus, for example, irradiation of 1a-d led to the formation of regioselective dibenzosemibullvalenes 2a-d in quantitative yields. However, irradiation of 1eunder similar conditions gave the corresponding dibenzodihydropentalenofuran derivative $3e^{4c}$ Interestingly, the thermal isomerization of the dibenzosemibullvalenes 2a-d gave the corresponding dibenzodihydropentalenofurans 3a-d in quantitative yields.^{4a,b} This thermal isomerization of dibenzosemibullvalenes is analogous to

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the vinylcyclopropane-cyclopentene rearrangement, which is known to occur thermally as well as photochemically.⁵

In the present study, we report the novel photochemical isomerization of the dibenzodihydropentalenofurans 3a-e to the corresponding dibenzosemibullvalenes 2a-e (Scheme 1). Earlier studies⁶ on the phototransformation of a few alkyl and phenyl substituted dihydrofuran derivatives such as 4 and 7 showed the formation of the corresponding regioisomeric mixtures of cyclopropyl ketones (5 and 6) and cyclopropyl aldehydes (8 and 9), respectively (Scheme 2), and these reactions are similar to the present photoisomerization. The basic difference between these substituted dihydrofurans and the dibenzodihydropentalenofurans is that, in the latter case, the yield of the photoisomerization products were found to be quantitative and only one isomer is formed due to the constraints of the polycyclic ring system. The present study provides a potential example of a photochromic system, in which both the thermal and the reversible photoisomerization reactions are very efficient (Scheme 1).

Another aspect of the present investigation deals with the study of ground-state triplet biradicals, involved in these photoisomerization reactions. Biradicals have been proposed as reaction intermediates in many thermal and photochemical reactions. Various aspects of both homoand heterosymmetric biradicals are well documented in the literature.⁷ The chemistry and kinetic behavior of photochemically generated biradicals have been areas of increasing interest in recent years.⁸ Several classes of biradical intermediates have been generated from a variety of precursors.⁹ For example, the Norrish Type I and Type II cleavages of ketones,¹⁰ photoinduced nitrogen elimination from azoalkanes,¹¹ and the photocleavage of strained ring compounds¹² have been extensively used to generate biradicals, and their photochemistry has also been reviewed in the literature.¹³ Also, much attention has been focused recently on understanding the multiplicity of these biradicals generated by different methods.¹⁴

Although the multiplicity of a biradical is controlled by the relative spin of the two electrons, which in turn is found to depend on several factors such as the throughspace interaction of the orbitals containing the unpaired electrons and the electronic effects of the substituents.^{14,15} For example, in biradicals if there is an effective throughspace interaction of the orbitals then a large HOMO– LUMO gap is generated. This large HOMO–LUMO gap can ultimately lead to a singlet state for the biradical. Similar singlet-state preferences have also been observed on substituting highly electronegative atoms between the radical centers, as in the case of cyclopentane-1,3-diyl biradicals.^{14,16} If, on the other hand, the HOMO–LUMO levels are nearly degenerate, then the resultant biradical will exist in the triplet state.^{7b}

The lifetime of a ground-state triplet biradical is governed by the intersystem crossing (ISC) efficiency to the singlet state. Spin–orbit coupling^{7a,17} and hyperfine

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coupling¹⁸ are primarily responsible for the ISC in triplet biradicals. Also, it has been observed that the lifetimes of triplet biradicals increase with electron withdrawing substituents and decrease with electron donating substituents, when attached to the radical centers.¹⁹ The triplet ground state of a diradical can be readily inferred by the temperature dependence of its lifetime as well as the Arrhenius factors, in addition to other spectroscopic and quenching studies.¹⁹ In the present investigation we have carried out the steady-state photolysis of dibenzodihydropentalenofurans 3a-e, and also have examined the nature of the transients involved in these rearrangements through nanosecond laser flash photolysis studies.

Results

The dibenzodihydropentalenofuran derivatives 3a-d were prepared by the thermal isomerization of the corresponding semibullvalenes 2a-d either under neat heating or by refluxing in a suitable solvent, as reported previously (Scheme 1).^{4a,b} However, **3e** was prepared by the steady-state photolysis of the corresponding dibenzobarrelene **1e**, at ambient temperature.^{4c} All the dibenzodihydropentalenofuran derivatives exhibited characteristic absorption maxima around 330 nm. Irradiation of the dibenzodihydropentalenofuran derivatives 3a-d using a RPR 350 nm light source gave the corresponding dibenzosemibullvalene derivatives 2a-d, in nearly quantitative yields (Scheme 1). The photoisomerization of 3e to 2e was monitored at low temperature (~15 °C), using ¹H NMR (300 MHz) spectroscopy since **3e** was found to revert back to 2e, at ambient temperature. Interestingly, the irradiation of **3e** at ambient temperature in benzene saturated with molecular oxygen led to the trapped endoperoxide 11e in good yield. The absorption maxima (around 255 nm) of dibenzosemibullvalenes are generally blue shifted in comparison to the corresponding dibenzodihydropentalenofurans.

These photoisomerization reactions were monitored by both UV and ¹H NMR spectroscopy and also by thin-layer chromatography, thereby excluding the possibility of other photoproducts in these cases. The spectral profile, as a function of irradiation time, for the isomerizaton of **3a** to **2a**, for example, is shown in Figure 1. Figure 1 reveals an isosbestic point around 280 nm, indicating the presence of only two species. The inset of Figure 1 shows the absorption spectrum of the photoproduct, dibenzosemibullvalene **2a**, indicating that the absorption maxima of the photoproduct and the starting material are well separated. The quantum yields for the photoisomerization of **3a**-**d** to the corresponding semibullvalenes **2a**-**d** were found to be in the range of 0.17-0.26 (Table 1).

Nanosecond laser flash photolysis studies revealed that the transient absorption spectra of the dibenzodihydropentalenofurans $3\mathbf{a}-\mathbf{e}$ in benzene show absorption maxima around 410 nm. Figure 2 shows the transient absorption spectra of $3\mathbf{a}$, as a representative example. The intrinsic lifetimes of the transients in benzene at 25 °C were found to be in the range 14–30 μ s and were sensitive to the presence of oxygen. The Stern–Völmer oxygen quenching constants for the biradicals derived



Figure 1. Irradiation profile of **3a**, recorded at each 30 s interval (irradiated with 350 nm monochromatic light source). The absorption at 335 nm (characteristic of **3a**) decreases with increase in irradiation time. Inset shows the UV absorption spectrum of **2a**.

from **3a**–**e** were in the range $2.45-3.17 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1). Both TEMPO ($k_q = 1.21 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in a representative case, **3a**) and HTEMPO weakly quenched the transients, and the rate constants were found to be in the range $1.09-3.19 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

The decay rates of the transients showed significant temperature dependence. The temperature effect on decay rate of the transient from 3a was studied in degassed toluene in the range of 30-70 °C (measured at each 10 °C increase). The decay rate was found to increase with temperature in an Arrhenius manner, and the Arrhenius parameters were calculated by linear regression method using standard equations. The activation energy for the transient from 3a was found to be nearly 4.35 ± 0.4 kcal mol⁻¹ and the Arrhenius preexponential factor (log A/s^{-1}) was 7.34 \pm 0.3. To examine the effect of the initial concentration on decay rate, the rates were monitored for solutions of different optical densities. It was found that the decay rate is independent of the initial concentration of the dibenzodihydropentalenofuran. An attempt was made to record the phosphorescence spectrum of **3a**, but it did not show any significant phosphorescence at 77 K in toluene-methylcyclohexane glass.²⁰

We assign the phototransients of dibenzodihydropentalenofurans (**3a**-**e**) as triplet biradicals on the basis of the following observations: (a) The biradical intermediate from **3e** was trapped by molecular oxygen to give the corresponding endoperoxide derivative **11e**. (b) The transients were quenched (trapped) by oxygen with rate constants in the range $2.45-3.17 \times 10^9$ M⁻¹ s⁻¹. (c) Both TEMPO and HTEMPO quenched the transients at higher concentrations with rate constants in the range $1.09-3.19 \times 10^6$ M⁻¹ s⁻¹. (d) The decay rates of these transients are independent of the initial concentration of the dibenzodihydrodpentalenofurans. (e) Decay rate shows significant temperature dependence and the Arrhenius preexponential factor (log A/s^{-1}) is relatively small (7.5, as in the case of **3a**, for example).

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Table 1. Lifetimes and Oxygen Quenching Constants of the Transients from the Dibenzodihydropentalenofurans 3a-e

compd	triplet birdical intermediate a $\lambda_{ m max}$, nm	lifetime (μ s) ^b	quenching constant, c $k(O_2)$, $10^9 M^{-1} s^{-1}$	quenching constant, ^d k(HTEMPO), $10^6 \mathrm{M}^{-1} \mathrm{s}^{-1}$	quantum yield e (ϕ)
3a	410	28.4 ± 1.3	2.45 ± 0.03	1.31 ± 0.03	0.26
3b	410	14.9 ± 0.60	3.04 ± 0.14	2.96 ± 0.19	0.17
3c	410	$24.5\pm0.1.2$	2.96 ± 0.10	3.19 ± 0.26	0.20
3d	420	30.7 ± 1.5	3.17 ± 0.12	1.40 ± 0.12	0.21
3e	410	11.7 ± 0.70	2.89 ± 0.13	1.09 ± 0.13	

^{*a*} The triplet biradicals were generated from the corresponding pentalenofurans by flash photolysis with a Nd:YAG 355 nm laser. ^{*b*} Mean value and standard error of samples of about 20–50 individual measurements in degassed benzene at 25 °C. ^{*c*} Determined by monitoring the decay rates in degassed, air-saturated, and oxygen-saturated benzene solutions and calculated using linear regression method. ^{*d*} Determined by adding known volumes of 0.5 M HTEMPO solution in benzene. TEMPO was also found to quench with similar rate constants. ^{*e*} Quantum yields for photoisomerization of the dibenzodihydropentalenofurans, determined by using azobenzene actinometry.³⁵



Figure 2. Transient absorption spectra of **3a**, in degassed benzene at 25 °C. Inset shows the decay monitored at 430 nm.

Discussion

The isomerization of dibenzosemibullvalenes 2a-d to the corresponding dibenzodihydropentalenofurans 3a-d takes place under thermal conditions and is analogous to the reported thermal ring-enlargement of vinylcyclopropanes to the corresponding cyclopentenes.⁵ The isomerization of vinylcyclopropanes to cyclopentenes is also reported to proceed through a singlet-state-mediated photochemical pathway.²¹ We have observed that the dibenzosemibullvalenes 2a - e are photochemically stable under our reaction conditions but thermally unstable.⁴ The thermal isomerization of dibenzosemibullvalenes can proceed through an adiabatic pathway involving the ground state potential energy surface and similar thermally reversible photoisomerizations are reported in the literature.²² The thermodynamic parameters of these isomerizations are in support of a concerted sigmatropic rearrangement, involving a cyclic transition state.^{4a,b,5} The driving force for the thermal isomerization can be the release of the strain energy associated with the fused cyclopropane ring system in the dibenzosemibullvalenes.

Interestingly, the dibenzodihydropentalenofurans 3a-e are thermally stable but photochemically isomerizable to the corresponding dibenzosemibullvalenes (2a-e). It is interesting to compare the photochemistry of the present system to that of 2-pyrazoline, where the photoisomerization was observed to be reversible even though the



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yields were not quantitative.²³ A probable pathway for the photoisomerization of dibenzodihydropentalenofurans **3a**-e to the corresponding dibenzosemibullvalenes **2a**-e is shown in Scheme 3, which involves the cleavage of the C–O bond, resulting in the formation of biradical intermediates **10a-e**. This mechanism is analogous to the photoisomerization of furan derivatives to the corresponding cyclopropene-3-carboxaldehydes.²⁴ For example, in the photoisomerization of furan, it has been suggested that the primary photochemical reaction step involves the cleavage of the C-O bond to generate a 1,5-biradical. This view was reasonably substantiated by theoretical calculations.²⁵ In this isomerization, the ground-state σ , π diradical, which is strongly stabilized by the pentadienetype resonance, is postulated as the precursor for the ring-closed cyclopropene-3-carboxaldehyde.

The dibenzodihydropentalenofurans under study (**3a**–**e**) can be viewed as aryl ketones, and hence, most likely the triplet excited states of these are involved in the photocleavage, to give triplet biradicals **10a**–**e**. Further transformation (ISC) of the triplet biradicals to the corresponding carbon centered singlet 1,3-biradicals would lead to the corresponding dibenzosemibullvalenes. Since no transients corresponding to the triplet excited states of the dibenzodihydropentalenofurans could be detected

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in the phosphorescence studies, it is assumed that a facile cleavage of the C-O bond occurs in the excited state to give the ground-state triplet biradicals.

While there are several reports for the photochemical ring cleavage of arylcyclopropane derivatives,²⁶ the dibenzosemibullvalenes, 2a-d under our irradiation conditions did not yield any photoproducts.²⁷ To probe the involvement of any phototransients in these cases, we have carried out some preliminary studies of a few dibenzosemibullvalenes (2c,d), through nanosecond laser flash photolysis technique. These compounds, on laser excitation ($\lambda_{exc} = 337.1$ nm) showed transients, with absorption maxima around 340 nm, which were not quenched by oxygen (see the Supporting Information). These transients are tentatively assigned as the corresponding singlet 1,3-biradicals,^{8b,16a,b} generated by the cleavage of the cyclopropyl σ -bond. The fate of the singlet biradical could be the coupling reaction to give back the semibullvalene derivatives, as we have not isolated any photoproduct under steady-state irradiation conditions of these cases.

The intrinsic lifetimes of the triplet biradicals generated from the dibenzodihydropentalenfurans (3a-e) are in the range $14-30 \ \mu s$. Adam and co-workers recently reported¹⁹ that the lifetimes of ground-state triplet biradicals are considerably enhanced by substitution of electron-withdrawing groups at the radical center, whereas the electron-donating substituents decreased their lifetimes. On the basis of this suggestion, it is of interest to compare the lifetimes of the triplet biradicals derived from the disubstituted dibenzodihydropentalenofurans 3c, 3d, and 3e. For example, 3c and 3d, where acetyl and benzoyl groups, respectively, are attached to the radical center, exhibited lifetimes of 24.5 and 30.7 μ s, respectively. On the other hand, for the diradical intermediate derived from 3e, in which the radical center is attached to the electron donating *p*-methoxyphenyl group, the lifetime was found to be 11.7 μ s, which is considerably lower in comparison to 3c and 3d. However, the appreciable difference in the lifetimes of the transients derived from monosubstitued dibenzodihydropentalenofurans 3a and 3b are rather difficult to rationalize. One possible explanation could be in terms of the electronic effects of the substituents. For example, in the case of **3b**, the electron withdrawing acetyl group can increase the HOMO-LUMO gap via the through-bond interaction and thereby resulting in a singlet preference for the biradical intermediate and consequent decrease in triplet lifetime (14.9 μ s), in contrast to the biradical derived from **3a** (28.4 µs).

Facile oxygen quenching and the isolation of the endoperoxide derivative 11e from the irradiation of 3e in the presence of oxygen strongly support the intermediacy of the triplet biradical species in the transformation of the dibenzodihydropentalenofurans (3a-e) to the corresponding semibullvalenes (2a-e). The observed oxygen quenching rate constants ((2.45–3.17) imes 10⁹ M⁻¹ s^{-1}) are in good agreement with the reported values for triplet cyclopentane-1,3-diyl biradicals.¹⁹ Further, these quenching rates are similar to those measured through different techniques such as photoacoustic calorimetry by Herman and Goodman $(5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{28}$ and Toscano and co-workers²⁹ using time-resolved infrared techniques (>2 \times 10⁹ M⁻¹ s⁻¹). The quenching of transients by TEMPO and HTEMPO, needs special mention. TEMPO and HTEMPO are known to quench both excitedstate triplets and also biradical intermediates.³⁰ For example, quenching rates of the excited-state triplets from dibenzobarrelenes³¹ by TEMPO and HTEMPO are in the range (0.24–0.43) \times 10 $^9~M^{-1}~s^{-1}$ and similar quenching rates were also observed for ground-state biradicals.³² However, there are also cases where similar nitroxyl radicals quench the biradicals at much lower rates $(1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$.^{9,33} In the case of the triplet biradicals derived from dibenzodihydropentalenofurans (3a-e), the quenching rate constants by TEMPO and HTEMPO were found to be considerably slower (1.09- $3.19 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$). The lack of effective quenching of the diradical intermediate 10a - e by these nitroxyl radicals could be attributed to steric hindrance near the radical sites.

The strong temperature dependence^{34,19} of the decay of the biradicals and a relatively small value of around 7.5 (characteristic of a spin forbidden process) for Arrhenius preexponential factor (log A/s^{-1}) obtained in the case of **3a** is in the range reported for ground-state triplet 1,3biradicals (6-10).¹⁹ The preexponential factor for the decay of singlet biradicals, on the other hand, falls in the range 10-14.^{15a} Therefore, the results of our quenching and kinetic studies are in support of the assignment of the transients as ground-state triplet biradicals.

Conclusions

In the present study, we have examined the photoisomerization of a few dibenzodihydropentalenofurans to the corresponding semibullvalenes, addressing the mechanistic aspects. Previously, we had reported the reverse thermal isomerization of the dibenzosemibullvalenes.^{4a,b} The photoisomerization of dibenzodihydropentalenofurans was found to proceed through biradical intermediates generated by the cleavage of the C-O bond. Based on quenching and kinetic studies the transients were assigned as ground-state triplet biradicals. The lifetimes of the biradicals were found to be influenced by substituents, attached to the radical centers. In a representative case, the biradical intermediate trapped with molecular oxygen to give the corresponding endoperoxide.

Experimental Section

The UV spectra were recorded on a Shimadzu UV-3010 PC NIR scanning UV spectrophotometer. The irradiation profile in Figure 1 was recorded with a solution of *n*-decane (\sim 5 \times

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⁽²⁷⁾ Wavelength-dependent steady-state irradiation of the dibenzosemibullvalenes was carried out using 254, 300, and 350 nm light source (RPR). No formation of the corresponding dibenzodihydropen-talenofuran derivatives was observed; only unchanged starting materials are isolated in quantitative yields.

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⁽³³⁾ Small, R. D., Jr.; Scaiano, J. C. Macromolecules 1978, 11, 840-841

⁽³⁴⁾ Buchwalter, S. L.; Closs, G. L. J. Am. Chem. Soc. 1979, 101, 4688-4694.

 10^{-4} M). The irradiation was carried out using Oriel optical bench, by using a 360 nm band-pass filter, in a quartz cell (6 \times 6 mm) at a distance of 30 cm from the light source. The quantum yield measurements were carried out using azobenzene as the actinometer.^{35}

General Procedure for the Steady-State Photolysis of Dibenzodihydropentalenofurans. A degassed solution of **3a**-**d** in benzene (100 mL) was irradiated in a Rayonet photochemical reactor (RPR 350 nm) at room temperature. The solvent was removed under vacuum, and the product thus obtained was recrystallized from a mixture (4:1) of dichloromethane and acetonitrile.

3a: irradiation of **3a** for 1 h gave a 94% of **2a**, mp 213-214 $^{\circ}$ C (mixture mp).

3b: irradiation of **3b** for 20 min gave a 96% of **2b**, mp 182–183° (mixture mp).

3c: irradiation of **3c** for 40 min to give 97% of **2c**, mp 181–182 °C (mixture mp).

3d: irradiation of **3d** for 40 min gave a 97% of **2d**, mp 192–193 °C (mixture mp).

Oxygen Trapping Experiments. A solution of 3e (200 mg, 0.38 mmol) in benzene (300 mL, dry) was saturated with oxygen and irradiated using a Hanovia 450 W lamp for 1.5 h, with continuous oxygen purging. The irradiated mixture, after removal of the solvent under reduced pressure, was chromatographed over silica gel by using chromatotron. Elution with a mixture (1:9) of ethyl acetate and hexane gave 90 mg (45%) of the starting dibenzodihydropentalenofuran derivative 3e, mp 168-169 °C (mixture mp), followed by 60 mg (29%) of the endoperoxide **11e**, mp 251–252 °C: IR v_{max} (KBr) 3075, 1695 cm⁻¹; UV λ_{max} (CH₃OH) 257 nm (ϵ 32, 400); ¹H NMR (C₆D₆) δ 3.18 (3H, s), 5.17 (1 H, s), 6.59-8.31 (22H, m); ¹³C NMR (C₆D₆) δ 54.62, 59.60, 84.38, 88.93, 105.01, 113.88, 121.14, 124.52, 125.69, 127.46, 127.70, 127.87, 128.02, 128.34, 128.75, 128.98, 130.28, 130.41, 131.23, 131.43, 132.87, 133.29, 133.54, 135.65, 141.32, 147.96, 150.87, 159.67, 191.69, 195.80; exact mol wt calcd for $C_{37}H_{26}O_5 (M + H)^+$ 551.1858, found 551.1849 (highresolution mass spectrometry).

Anal. Calcd for $C_{37}H_{26}O_5\!\!:$ C, 80.73; H, 4.72. Found: C, 80.34; H, 4.92.

The experiment was also monitored by $^1\!H$ NMR spectroscopy in $C_6D_6,$ by irradiation using an Oriel optical bench under identical conditions.

¹H NMR Monitoring of the Photoreactions of 3a-d. A solution of 3a-d in C_6D_6 (10 mg in 0.5 mL) in an NMR tube was degassed for 10 min and irradiated using an RPR 350 nm light source for 20 min, and its ¹H NMR spectrum (300 MHz) was recorded. The photoconversion was monitored by observ-

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ing the bridgehead and/or the alkyl protons. However, in the case of **3e**, the irradiation was carried out at ${\sim}15$ °C and the spectrum was recorded immediately.

Laser Flash Photolysis Studies. Nanosecond laser flash photolysis studies were performed using a Laser Photonics PRA/model UV-24 nitrogen laser system (337.1 nm, 2 ns pulse width, 2–4 mJ/pulse) and/or by the third harmonic laser pulse from a Nd:YAG laser GCR-12 series, Quanta Ray (355 nm, 10 ns pulse width, ~70 mJ/pulse). A kinetic absorption spectrometer (LKS-20 Applied Photophysics) has been used to detect the changes in optical density, after the laser excitation. A typical experiment consisted of several replicate shots per single measurement. The intrinsic lifetimes were measured in benzene, at 25 °C, after purging with argon for 30 min. Oxygen quenching constants were determined by monitoring the decay rates of the respective substrates in air and oxygen saturated benzene solutions. Quenching studies using HTEM-PO were carried out by following the decay rates, after the addition of calculated amounts of a 0.5 M solution of the quencher in benzene. The transient absorption spectra were recorded in degassed benzene, using a flowcell. The optical density of the dihydrodibezopentalenofurans solutions at 355 nm was in the range 0.5-1.5.

The kinetics of the triplet decay were studied over the temperature range of 30-70 °C, and the desired temperature was achieved by circulating water through the cell jacket. The temperature inside the cell was calibrated using a digital thermometer. The activation energy and Arrhenius collision factor were evaluated using linear regression method by applying standard equations.

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Supporting Information Available: Transient absorption spectra of **3b**–**e**, Stern–Völmer oxygen quenching plots (**3a**–**e**), and HTEMPO quenching plots (**3a**–**e**), ¹H, ¹³C, DEPT-135 NMR spectra of **11e**, Arrhenius plot for the decay of the transient from **3a**, and transient decay and transient absorption spectra of **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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