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Rapidly Rearranging Excited States of Bichromophoric Molecules—Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: The photochemistry of 4,4-di(α-naphthyl)-2,5-cyclohexadienone and 4,4-di(β-naphthyl)-2,5-cyclohexadienone was investigated. The α-dienone rearranged with a quantum efficiency of 1.00 to afford 3,4-di(α-naphthyl)phenol as opposed to the usual type A rearrangement followed by virtually all 2,5-cyclohexadienones. Both direct and sensitized reactions led to this product and with the same efficiency. In contrast, the β-dienone gave both types of products—aryl migration and type A. 3,4-Di(β-naphthyl)phenol and 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one were formed on direct irradiation with quantum yields of ϕ = 0.61 and 0.38, respectively. This was quite different from the sensitized photochemistry where aryl migration occurred almost exclusively (94%); the xanthone-sensitized efficiency was 0.96 for formation of the 3,4-di(β-naphthyl)phenol and 0.04 for the 6,6-di(β-naphthyl)bicyclic ketone. Sensitization with thioxanthone (66 kcal/mol), having an energy intermediate between the naphthyl (61 kcal/mol) and cyclohexadienone (69 kcal/mol) moieties, led to the same product distribution and efficiencies as xanthone (74 kcal/mol). A third mode of excited-state generation was devised with use of dioxetane derivatives of the α- and β-dienones, the idea being to inject triplet excitation at the locus of the carbonyl group. This approach afforded the same qualitative and quantitative results as the direct irradiations, thus suggesting that in the direct irradiations triplet excitation is localized near the carbonyl moiety at the moment of intersystem crossing. Hence direct irradiation and dioxetane approaches differ from the sensitizations where triplet excitation is delivered selectively to the naphthyl groups. Both the α- and the β-dienones were quenched with cyclohexadiene. A linear Stern–Volmer plot was observed for the α-dienone. For the β-reactant, the ϕ₀/ϕ plot of bicyclic ketone was also linear; dramatically, the plot for the phenolic product was linear with a large slope at low quencher concentration and linear, however, with a small slope, at high quencher concentration. Kinetic analysis of the slopes for the β-dienone led to the same lifetime for the short-lived triplet whether this was based on the bicyclic ketone plot or the phenol plot. At most, minor fluorescence quenching was encountered under conditions of these studies, and the short-lived species therefore was a triplet. It was assigned an n–π* configuration. Rates were determined for the various reaction and decay processes in the α- and β-series. Interestingly, the main reaction product of the β n–π* triplet is bicyclic ketone while the major product of the naphthyl-localized π–π* triplet is virtually exclusively the 3,4-phenol. In the α-series, both triplets lead to phenolic product.

In our recent research[2,3] we have encountered examples of 4,4-diarylcyclohexenone rearrangements where the rate of energy equilibration between aryl and carbonyl chromophores is rapid compared to the rate of rearrangement. An intriguing prospect was the study of cases with more rapidly rearranging triplets, so that the rate of energy equilibration would be slower than the rates of reaction of the two discrete excited states. The type A cyclohexadienone rearrangement[4] promised to provide such a reaction. Consequently, the investigation of the photochemistry of 4,4-di(α-naphthyl)cyclohexadienone (**1**) and 4,4-di(β-naphthyl)cyclohexadienone (**2**) was initiated.

Results

Synthetic Aspects. The requisite α- and β-cyclohexadienones **1** and **2** were synthesized from the corresponding dinaphthyl-cyclohexanones[2] **3** and **4**, respectively, as outlined in Scheme I. Scheme I also includes the synthesis of the 4,5-di(α- and β-naphthyl)cyclohexan-1,3-diones **9** and **10**. These diones were needed for the synthesis of potential photoproducts (vide infra).

One interesting facet involved the Michael addition reaction of naphthyl acetates (e.g., **12**) and naphthylacetones (e.g., **6**) to

acceptors such as **11** and **15**. While the β-naphthylacetate methyl ester **12** added nicely in Michael fashion to enone **11**, the corresponding reactions in the α-naphthyl series proved fruitless. Not only did unsaturated ketone **13** and ester **14** not react but also the alternative pair—**15** and **6**—were unreactive. The problem seemed a consequence of the greater steric hindrance provided by an α-napthyl group. The dilemma was circumvented by use of a more reactive Michael acceptor, the unsaturated malonate derivative **5**.

Scheme II delineates the conversion of the 1,3-diones to dinaphthylphenols, which were deemed to be potential photoproducts and therefore requiring synthesis.

Finally, there were grounds for believing that a synthesis of 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one (**34**) was desirable. We noted that the corresponding 6,6-diphenyl analogue **36** is the primary photoproduct of the irradiation[4] of 4,4-diphenylcyclohexadienone (**35**) as shown in eq 1. The synthesis of the 6,6-
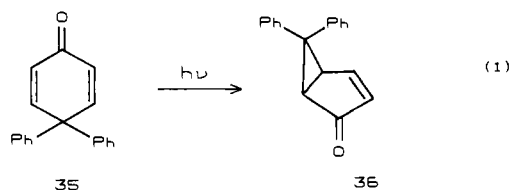
di(β-naphthyl)bicyclic ketone **34** is outlined in Scheme III. The reaction of diaryldiazomethanes with cyclopent-4-ene-1,3-diones has proven of general value.[5]

A final point of interest is the acid-catalyzed dienone–phenol rearrangement[6] of the 4,4-di(α- and β-naphthyl)cyclohexadienones

(1) This is paper 146 of our photochemical series and 204 of our general series.
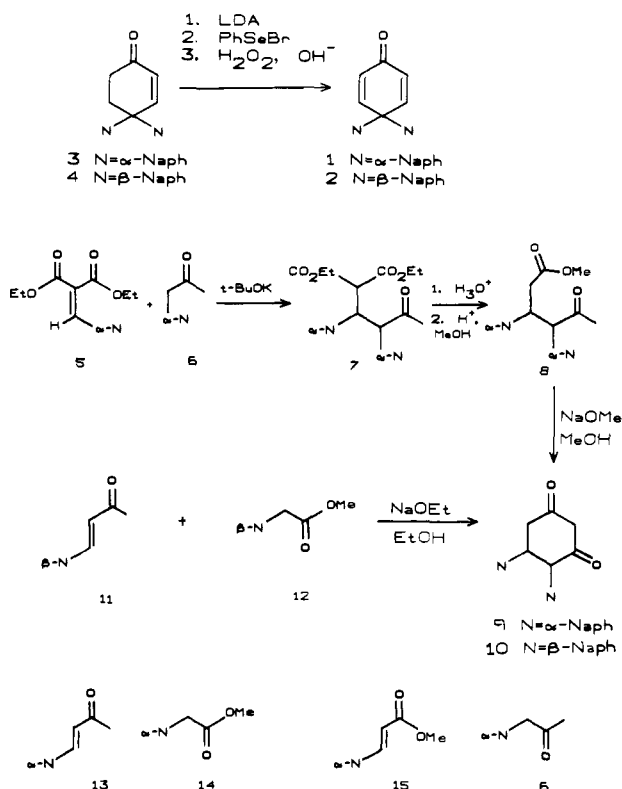
(2) For paper 145 note: Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732–7744.

(3) Zimmerman, H. E.; Xu, J.-H.; King, R. K.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724–7732.

(4) (a) Zimmerman, H. E. Seventeenth National Organic Symposium of the American Chemical Society, Bloomington, Indiana, 1961; pp 31–41. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527–4540. (c) "A New Approach to Mechanistic Organic Photochemistry"; Zimmerman, H. E. In "Advance in Photochemistry"; Noyes, A., Jr., Hammond, G. E.; Pitts, J. N., Jr. Eds.; Interscience: New York, 1963; Vol. 1, pp 183–208. (d) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906–912. (e) Note also ref 5 for a recent study.

(5) (a) Zimmerman, H. E. Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864–4875. (b) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876–4891.

Scheme I. Synthesis of the Dienones and the 4,5-Dinaphthyl Cyclohexan-1,3-diones

1. LDA
2. PhSeBr
3. H_2O_2, OH^-

3 N=α-Naph
4 N=β-Naph

1 N=α-Naph
2 N=β-Naph

CO_2Et CO_2Et

5   +   6   →   t-BuOK   →   7
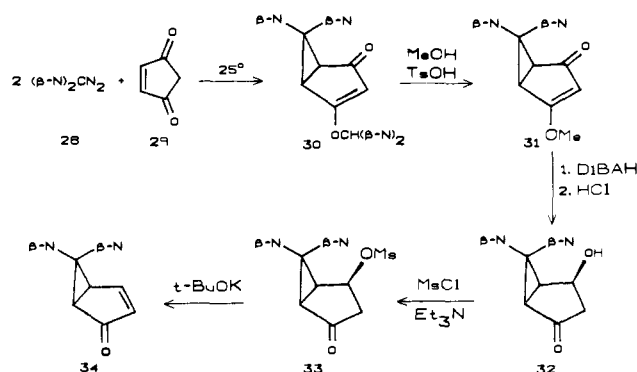
1. H_3O^+
2. H^+, MeOH

8

NaOMe
MeOH

11   +   12   →   NaOEt / EtOH   →

9 N=α-Naph
10 N=β-Naph

13   14   15   6

Scheme II. Conversion of the 1,3-Diones to the Dinaphthyl Phenols

H^+, CH_3OH →

OCH₃

9 N=α-Naph
10 N=β-Naph

16 N=α-Naph
17 N=β-Naph

18 N=α-Naph
19 N=β-Naph

1. LAH
2. H_3O^+ →   DDQ   →

16 N=α-Naph
17 N=β-Naph

20 N=α-Naph
21 N=β-Naph

22 N=α-Naph
23 N=β-Naph

1. LAH
2. H_3O^+ →   DDQ   →

18 N=α-Naph
19 N=β-Naph

24 N=α-Naph
25 N=β-Naph

26 N=α-Naph
27 N=β-Naph
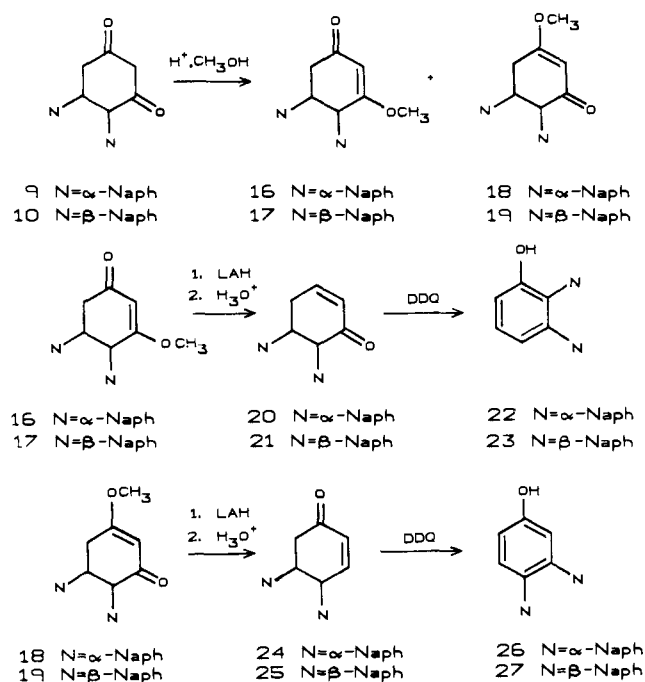
1 and 2. Each dienone rearranged cleanly to the corresponding 3,4-dinaphthylphenol (i.e., **26** and **27**); note eq 2. However, the conditions required for the rearrangements differed markedly, with the α derivative rearranging under very mild treatment where the β-dienone was stable. The considerable difference in facility of rearrangement, no doubt, arises from a greater delocalization of

Scheme III. The Synthesis of 6,6-Di-(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one

2 (β-N)₂CN₂ + 28   29   →   25°   →   30   →   MeOH / TsOH   →   31

1. DiBAH
2. HCl

34   ←   t-BuOK   ←   33   ←   MsCl / Et₃N   ←   32

the species having an α-naphthyl group bridged between C-4 and C-3 of the oxygen-protonated dienone moiety.

H_3O^+ →   (2)
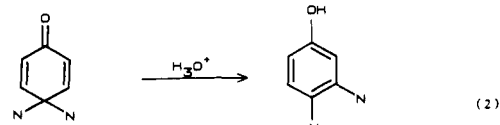
1 N=α-Naph   mild conds.
2 N=β-Naph   harsh conds.

26 N=α-Naph
27 N=β-Naph

Mild Conditions: HOAc, 80°, 10 min. Reaction of the α-Isomer but no reaction for the β-Isomer under these conditions. Harsh Contions: 10% conc HCl in HOAc. 5 hr. 110° required for the β-Isomer

Exploratory Photochemistry of the Dienones. Both direct and xanthone-sensitized irradiation of the 4,4-di(α-naphthyl)cyclo-hexadienone **1** led with extreme facility to a single photoproduct; this proved identical with the 3,4-di(α-naphthyl)phenol **26** already synthesized. Since 2,3-diarylphenols, as well as the 3,4-isomers have been observed as secondary photoproducts in our earlier efforts,[5,7] runs were made to lower conversions. However, none of the 2,3-di(α-naphthyl)phenol **22** was observed, and no bicyclo[3.1.0]-type products (e.g., **36**) were detected. Thus it appeared that the di-α(naphthyl)phenol **26** was a primary photoproduct. This point is considered in more detail below. The photochemistry of the 4,4-di(α-naphthyl) dienone **1** is depicted in eq 3.

hν
CH_3CN
dir or sens

(3)

1   26
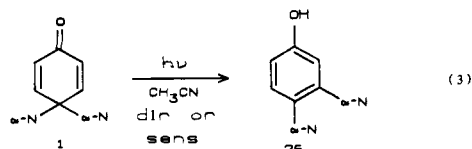
Turning to exploratory direct irradiations of the 4,4-di(β-naphthyl) dienone **2**, we observed two photoproducts, both of which proved from lower conversion runs to be primary. These were formed in a ca. 3:2 ratio. The major photoproduct was found to be identical with the synthetic 3,4-di(β-naphthyl)phenol **27** (vide supra), and the latter was the 6,6-di(β-naphthyl)bicyclic ketone **34** also previously synthesized. Remarkably, the direct photochemistry introduced no complications due to secondary reactions of the type encountered in the diphenyl system. This appears due to the low reactivity of the primary photoproducts.

In contrast, the xanthone (E_T = 74 kcal/mol[8]) and thioxanthone (66 kcal/mol[9]) sensitized reactions of the di(β-naphthyl) dienone **2** led almost exclusively to the 3,4-di(β-naphthyl)phenol **27** with observation of the 6,6-di(β-naphthyl)bicyclic ketone **34** in minor amounts. The ratio of phenol **27** to bicyclic ketone **34** was close to 24:1, independent of sensitizer and extent of conversion. Again, these products proved to be primary.

(6) (a) Dreiding, A. S.; Pummer, W. J.; Tomasewski, A. J. *J. Am. Chem. Soc.* **1953**, *75*, 3159–3161. (b) von Auwers, K.; Ziegler, K. *Annalen* **1921**, *425*, 217–280.

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(8) Pownall, H. S.; Huber, J. *J. Am. Chem. Soc.* **1971**, *93*, 6429–6436.

(9) Herkstroeter, W. G.; Lamola, A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537–4540.
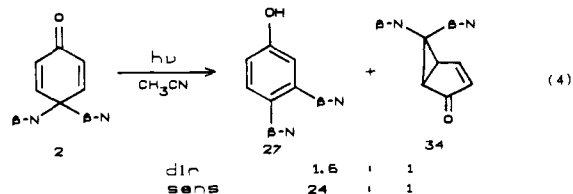
Table I. Quantum Yields[a,b]

reactant	sensitizer	wavelength, nm	quantum efficiency	
			phenol	bicyclic
α-dienone	none	313	1.00	0.00
α-dienone	xanthone	340	1.00	0.00
β-dienone	none	313	0.61	0.38
β-dienone	xanthone	313	0.96	0.04$_2$
β-dienone	thioxanthone	334	0.96	0.04$_4$

[a] Solvent acetonitrile. [b] Error limits ±5% except ±10% for bicyclic product from sensitized runs.

The direct and sensitized photochemical transformations of the 4,4-di(β-naphthyl) dienone **2** are depicted in eq 4.

$$\text{(4)}$$

	dir	sens
	1.6	24
	1	1

Quantum Yield Determinations. Quantum yields were determined with use of the microbench apparatus described previously.[10] Both direct and sensitized efficiencies are given in Table I. The remarkable observation was the very large quantum efficiencies encountered throughout. A second observation was an identity of the direct and sensitized quantum yields in the case of the di(α-naphthyl) dienone **1**. This provided necessary but not sufficient evidence that in the α series the rearrangements in the direct irradiations were occurring via a triplet excited state. Furthermore, we can conclude that any state of the α isomer reacting, singlet or triplet, must do so with unit efficiency and that any intersystem crossing also must be perfectly efficient.

The differing product distributions from the β-dienone in the direct and sensitized runs indicate that two different species are involved. These might be T_1 and S_1 or T_1 and T_2; this is considered below. Also, there was the remarkable observation that both xanthone (74 kcal/mol) and thioxanthone (66 kcal/mol) afforded dinaphthylphenol product **27** with 0.96 efficiency. The choice of thioxanthone was suggested by its energy being between that of the 61 kcal/mol[11] naphthyl moiety and that of the 69 kcal/mol cyclohexadienone chromophore.[12] Again, any intersystem crossing must be perfectly efficient to account for the total quantum yield of 0.99.

Absorption, Fluorescence, and Phosphorescence Measurements. The ultraviolet absorption spectrum of the β-naphthyldienone **2** was unexceptional, being approximately the superposition of dienone and naphthyl chromophores; note Figure 1. However, the spectrum of the α-isomer **1** showed enhanced absorption attributable to 1,3 overlap between the β carbon of the enone moiety and carbon-1 of the α-naphthyl group. The α-naphthyl dienone exhibited virtually no fluorescence, hence not permitting a second check on π–π coupling in the singlet manifold. However, the β-dienone showed modest fluorescence with 0–0 emission at 325 nm corresponding to the 322-nm fluorescence of naphthalene, itself.[11a] The fluorescence quantum yield was measured as 0.023 ± 0.003. Considering the sum of the two reaction quantum yields as 0.99 ± 0.015, it is seen that the sum of the reaction quantum yield and fluorescence is near unity and signifies the unimportance of nonradiative decay processes. From the practical standpoint, the 0.023 fluorescence efficiencies permitted its monitoring with facility.

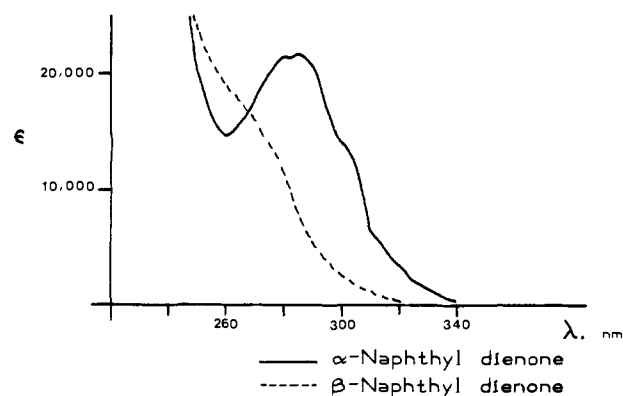Thus the β-dienone shows no conjugative interaction between
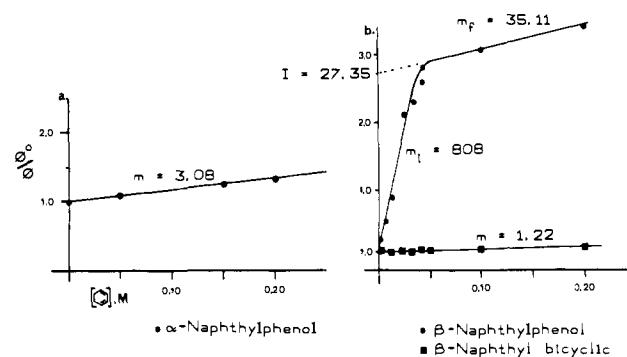
Figure 1. Ultraviolet spectra of dienones.

Figure 2. Stern–Volmer quenching plots.

dienone and naphthyl chromophores.

The fluorescence was also monitored with added cyclohexadiene with concentrations of diene corresponding to those used in triplet quenching studies (vide infra). It was important to ascertain if singlet quenching was occurring. However, under these conditions at most only minor (<7%) fluorescence quenching was observed while bicyclic product was quenched over 50%.

The phosphorescence spectra revealed 0–0 peaks at 492 nm (58.2 kcal/mol) in the case of the α-dienone **1** and 487 nm (58.8 kcal/mol) for the β-dienone **2**. These values are close to that of naphthalene which has T_1 at 61 kcal/mol[11b,c] and much lower than the 69 kcal/mol T_1 energy of cyclohexadienones.[12] Hence the lowest triplets appear to have their excitation heavily localized in the naphthyl moiety with no indication of coupling of chromophores.

Quenching Studies. The sensitization results presented (vide supra) provided necessary but not sufficient evidence that triplets might be the reacting species in the photochemistry of the α-dienone **1**. For the β series the product dependence on mode of excitation indicated two excited species being responsible for the observed photochemistry. In order to provide further indication of the multiplicity of the excited states reacting, quenching studies were undertaken.

Stern–Volmer plots were obtained with 1,3-cyclohexadiene (E_T = 53 kcal/mol[13]); note parts a and b of Figure 2. The plot for the α isomer was linear with a slope corresponding to a $k_q\tau$ value of 3.08 L mol^{-1}. Using a value[14] of 1.1×10^{10} L mol^{-1} s^{-1} for k_q = k_{diff} (in acetonitrile) led to a triplet lifetime of 0.28 ns, corresponding to a unimolecular total rate of triplet decay, $k_{d(tot)}$, of 3.6×10^9 s^{-1}. The relation $k_r = \phi_r k_{d(tot)}$ thus affords a triplet reaction rate of 3.6×10^9 s^{-1} since the quantum yield is unity. The quenching and rate data are summarized in Table II.

Similarly, a ϕ_0/ϕ plot for the β-bicyclic product **34** vs. quencher

(10) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.
(11) (a) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1965. (b) Marichetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768–777. (c) Terenen, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1043–1052.
(12) Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 6589–6595.

(13) (a) Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4230–4238. (b) Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4781–4782.
(14) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898–5901.
(15) Schuster, D. I.; Lau, N. K. *Mol. Photochem.* **1969**, *1*, 415–432.

Table II. Quenching and Rate Data

reactant triplet(s)	photoproduct	ϕ	τ, ns	$k_{d(tot)}$, s^{-1}	k_r, s^{-1}	k_d, s^{-1}
α-dienone^a n-π^*, π-π^*	phenol **26**	1.00	0.28	3.57 × 10^9	3.57 × 10^9	0.00 × 10^9
β-dienone^a π-π^*	phenol **27**	0.59	74.0	1.36 × 10^7	8.03 × 10^6	5.57 × 10^6
β-dienone^a n-π^*	phenol **27**	0.020	0.11	9.01 × 10^9	1.80 × 10^8	5.41 × 10^9
β-dienone^a n-π^*	bicyclic **34**	0.38	0.11	9.01 × 10^9	3.42 × 10^9	5.41 × 10^9
diphenyl dienone^{b,c} n-π^*	bicyclic **36**	0.85	0.08	1.25 × 10^{10}	1.06 × 10^{10}	1.90 × 10^9

^{a}Solvent acetonitrile. ^{b}Benzene. ^{c}Reference 15.

concentration was linear as depicted in Figure 2b. The corresponding data are given in Table II.

Interestingly, the quenching plot for the β-dienone **2** revealed two linear regions with different slopes when ϕ_0/ϕ was plotted for the 3,4-di(β-naphthyl)phenol **27**. Such behavior is characteristic of the intervention of two species, both responsible for the observed product but having different lifetimes. The two species here, a priori, could be a singlet and a triplet or two different triplets.

However, as stated above, under the conditions of the quenching studies, it was found that the β-naphthyl reactant's fluorescence was not appreciably quenched; note the Experimental Section. Hence, the species being quenched cannot include the singlet excited states. Rather these must include n-π^* and π-π^* triplets (vide infra). Also, this conclusion is in agreement with the dioxetane experiments described below.

As has been noted by Wagner,[16a] the individual slopes of such dual slope plots cannot be directly equated to $k_q\tau$ as in simpler examples. Rather, the initial slope (m_i), the final slope (m_f), and the intercept (I) are given by eq 5–7 based on the assumption of no conversion of the lower to the upper state.

$$m_f = (1 + R)L_2 \quad (5)$$

$$m_i = L_2 + RL_1/(1 + R) \quad (6)$$

$$I = (1 + R)(1 - RL_2/L_1) \quad (7)$$

where $R = \phi_1/\phi_2$, $L_1 = k_{q1}\tau_1$, and $L_2 = k_{q2}\tau_2$

While eq 5–7 were derived for the case of one singlet plus one triplet, they are equally validly applied to T_1 plus T_2 situations. Thus here the subscripts 1 and 2 refer to T_1 and T_2, respectively.

An analytical solution for the $k_q\tau$ values is readily obtained.[16c] Thus,

$$k_{qx}\tau_x = [1/2(I - 1)][(m_iI - m_f) \pm \text{root}] \quad (8)$$

where

$$\text{root} = [(m_iI - m_f)^2 - 4(m_im_f - m_f^2)(I - 1)]^{1/2} \quad (9)$$

Here the plus sign in eq 8 gives the $k_q\tau$ value for T_1 (i.e., $x = 1$) and the minus sign affords the $k_q\tau$ value for T_2 (i.e., $x = 2$).

Similarly, the relative reaction efficiencies using the two triplets are given by

$$\phi_2/(\phi_1 + \phi_2) = L_2/m_f = k_{q2}\tau_2/m_f \quad (10)$$

It is reasonable to take both quenching constants, that for T_1 and that for T_2, to be diffusion controlled. In confirmation of the validity of this treatment, the T_2 τ value of 0.11 ns obtained from this treatment of the 3,4-di(β-naphthyl)phenol formation agrees nicely with the value obtained by using the simple treatment of the single slope observed for the β-naphthylbicyclic ketone (compare τ for entries 3 and 4 of Table II).

Dioxetane Thermolyses. The evidence thus far suggested the intervention of two triplets in the photochemistry of the β-dienone **2**. It appeared likely that in T_1 the β-naphthyl moiety was excited (61 kcal/mol) while in T_2 the 2,5-cyclohexadienone chromophore

possessed an n-π^* configuration (69 kcal/mol). In the α-dienone photochemistry the same product was encountered independent of mode of triplet generation. Although in this case there was no suggestion of the presence of two triplets, the same two configurations were a priori candidates for the observed photochemistry.

A particularly intriguing approach to determining the role of the two potential triplets was the selective excitation of one of the two chromophores by dioxetane thermolysis to afford an excited dienone moiety.[17]

To this end we synthesized the dimethyl dioxetane **40** corresponding to the α-naphthyl dienone **1**. We utilized the singlet oxygen reaction of the di(α-naphthyl)isopropylidene diene **38**, a method having precedent in our earlier work;[17] note eq 11. The same method was successful in preparing the β-napthyldioxetane **41**. Both of these were nicely crystalline and relatively stable compounds in the solid state.

1 N=α-Naph   38 N=α-Naph   40 N=α-Naph
2 N=β-Naph   39 N=β-Naph   41 N=β-Naph

(11)
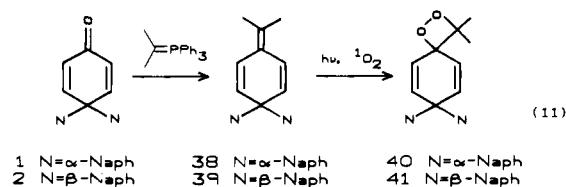
The dark thermolysis of these dioxetanes was effected in acetonitrile at 82 °C. The β-dioxetane **41** afforded, in addition to di(β-naphthyl) dienone **2**, the 3,4-di(β-naphthyl)phenol **27** and the di(β-naphthyl)bicyclic ketone **34** in a 1.6:1 ratio. Interestingly, this ratio is the same as obtained (vide supra) in the direct irradiation of the di(β-naphthyl) dienone **2**. Since dienone dioxetane thermolyses primarily afford triplets,[17] this result confirms the conclusion from the lack of fluorescence quenching that the Stern–Volmer quenching involves two triplets rather than a singlet and a triplet. Equation 12 depicts the dioxetane thermolysis.

The corresponding dark thermolysis of the α-dioxetane **40** led only to α-naphthyl dienone **1** and the di(α-naphthyl)phenol **26**. The latter was, again, the product of direct irradiation of the corresponding dienone. This transformation is shown in eq 13.

41   2   27   34

Product Ratio •   94.8   :   3.2   :   2.0

(12)

40   1   26

Product Ratio •   79   :   21

(13)
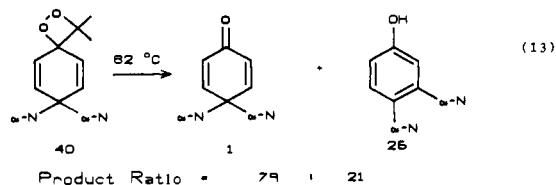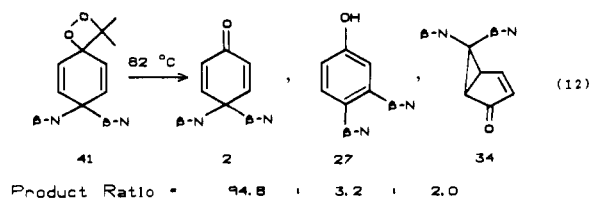
Interpretative Discussion

The Overall Reaction Course. One of the most striking observations in this study was the occurrence of the aryl migrations intervening both in competition with and in place of the ubiquitous[4,18] type A (i.e., Lumi) rearrangement, a transformation commonly accepted[18d] as deriving from the n-π^* triplet. There

(16) (a) Wagner, P. J. In "Creation and Detection of the Excited State"; Lamola, A. A., Ed.: Dekker Inc.: New York, 1971; pp 173–212 (note also ref 16b). (b) A parallel relationship in different form has been described by Shetlar (Shetlar, M. *Mol. Photochem.* **1973**, *5*, 311–326 (note especially p 314)). (c) The present equation arises from a solution of the equations in ref 16a for the τ's (note Appendix).

Excited States of Bichromophoric Molecules

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are few examples of dienones and their derivatives undergoing an aryl migration. In one such case, 4-aryl-substituted naphthalenones afford α-naphthols.[19] In one other, 3-methoxy-4,4-diphenyl-2,5-cyclohexadienone (**42**) afforded[5] ca. 20% of 3-methoxy-4,5-diphenylphenol (**43**) along with the usual bicyclo[3.1.0]hex-3-en-2-one (i.e., type A) products. In the naphthalenone case, the reactant is not strictly a dienone. In the 3-methoxydienone **42** example, the methoxy substitution lowers the energy of the $\pi-\pi^*$ triplet sufficiently to permit reactivity competitive with the normal $n-\pi^*$ type A rearrangement.

In the present instance, an initial interpretation might be either (a) that one is observing intervention of $\pi-\pi^*$ reactivity in view of the low triplet energy (ca. 61 kcal/mol) of the naphthyl moiety or (b) that the facility of aryl migration from C-4 to C-3 is greatly enhanced in the case of C-4 naphthyl substitutents. In our earlier efforts[3,19,20] it was, indeed, observed that phenyl groups substituted with methoxyl, cyano, or phenyl had enhanced migratory aptitudes. Even more cogently, in our recent study of naphthyl-substituted cyclohexenones,[2] enhanced quantum yields, and triplet rates, compared with the phenyl analogues, were observed; here α-naphthyl proved to migrate with greater facility than β-naphthyl. Accordingly, the deviation from total type A rearrangement, as depicted in eq 3 and 4, seems reasonable, although the mechanistic details still need to be elaborated.

Significance of the Efficiencies and Kinetic Observations. The first consequence of the unit efficiencies is the certainty that all of the photochemistry is primary; any two-step photochemistry would lead to lower quantum yields.

Further, such high quantum yields are relatively rare. While type A rearrangements characteristically have high efficiencies,[4,5,21] quantum yields totalling unity for all reactions in the present study signify the presence of more than one facile excited-state process.

Inspection of the Stern–Volmer plots of Figure 2 is helpful. Let us begin with consideration of the β-dienone. Thus, we might begin with the tentative assumption, using analogy with known photochemistry, that the type A process affording bicyclic ketone product **34** originates from the $n-\pi^*$ triplet. The small slope for this plot in Figure 2b suggests a very short-lived species; this presumption was confirmed by the kinetic treatment given in the Results Section and leading to the 110 ps τ value listed in Table II.

We now focus attention on quenching the formation of β-naphthylphenol **27**. We have already noted (vide supra) that the dual slopes of this curve in Figure 2b point to intervention of two discrete triplet excited states leading to this photoproduct. The triplet being quenched with a steep slope is a long-lived one (74 ns, note Table II) while that being quenched inefficiently (i.e., with a small slope) is a short-lived one (i.e., 110 ps). If the short-lived triplet is, indeed, to be taken as $n-\pi^*$, then by default the long-lived triplet may reasonably be taken as $\pi-\pi^*$ wherein a β-naphthyl group is excited. In addition, we see from the Stern–Volmer treatment and results in Table II that β-naphthyl migration occurs to a minor extent from the $n-\pi^*$ excited state as well; this corresponds to the small-slope portion of the Stern–Volmer plot and thus to the 110-ps lifetime triplet. The identity of the naphthylphenol forming triplet lifetime of 110 ps with the

lifetime of the type A precursor supports this interpretation.

Turning to the quite linear Stern–Volmer treatment of the α-naphthyl dienone **1**, as given in Figure 2a, we conclude either that only a single reactive excited state is being quenched or, alternatively, that two rapidly equilibrated excited states are involved, with either one or both reacting. The kinetics of energy equilibration and reaction of bichromophoric rearranging molecules has been discussed in detail earlier.[2,14]

The Three Approaches to Electronic Excitation and Their Interrelation. With maximum conclusions drawn from photochemistry under quenching conditions, we sought alternative approaches to determining which two excited states were involved and for what photochemical behavior each was responsible. Here we focus attention on the product distribution as a function of mode of triplet generation. It is clear that the product distribution is determined by three factors. The first is initial partition of excitation between different excited states. The second factor is subsequent redistribution of energy among chromophores. The third is the distribution of products from each state so generated. Relative to the last of three factors the Stern–Volmer treatment (note Table II especially) provides information on the reaction selectivity of each triplet.

A particularly intriguing attack on the problem came from the use of dioxetanes. In some of our earlier studies,[17] we generated the $n-\pi^*$ triplet excited state of 4,4-diphenylcyclohexadienone by dioxetane thermolysis without light. While one might question[22] the certainty that it is an $n-\pi^*$ configuration which is generated specifically in such thermolyses, the initial locus of excitation being in the vicinity of the carbonyl chromophore should not be in doubt. Accordingly, the product distribution in the dark thermolysis of the β-naphthyldioxetane defines the behavior of the β-naphthyldienone **2** when the dienone chromophore is excited to the triplet, and the type A reactivity characterizes the triplet as $n-\pi^*$. As noted in eq 12 of the Results Section, the dioxetane thermolysis products consisted of di(β-naphthyl)phenol **27** and di(β-naphthyl)bicyclic ketone **34** in a 1.6:1 ratio in addition to the β-naphthyl dienone **2** recovered. (Throughout the following discussion, the mention of the products of dioxetane thermolyses does not include recovered dienone but only products of the triplet generated.)

Interestingly, although our dioxetane triplet excitation originates near the carbonyl group, the predominant product (ca. 3:2) is not the typical $n-\pi^*$ type A bicyclic ketone, but rather the dinaphthylphenol resulting from aryl migration.

That the same approach, utilizing dioxetane thermolysis to inject triplet excitation in the locale of the dienone moiety of α-naphthyl dienone **1**, led (vide supra) to the 3,4-di(α-naphthyl)phenol **26** has two interpretations. The first is that the α-dienone $n-\pi^*$ excited state reacts in a fashion atypical for a dienone. The second is that energy transfer from the dienone moiety to the α-naphthyl group is more rapid, relative to the type A rearrangement, than in the β counterpart. In either case, the Stern–Volmer treatment, which reveals a single triplet lifetime, demands either a single triplet being responsible for all the reactivitiy in the α-naphthyl dienone photochemistry or a fortuitous coincidence of the lifetimes of the $n-\pi^*$ dienone-localized triplet and the $\pi-\pi^*$ naphthalene localized triplet. We do know that α-naphthyl migrates to the β carbon of an excited enone moiety with greater facility (ca. 3-fold) than a β-naphthyl moiety does,[2] and in the β-naphthyl dienone the $n-\pi^*$ excited state does exhibit some (ca. 6% of the total $n-\pi^*$ reaction; note Table II) naphthyl migration.

The second mode of excited-state generation was direct irradiation. The product distributions, both for the α-naphthyl and for the β-naphthyl dienones **1** and **2**, were the same as from the dioxetane triplet generation. Particularly, in the case of the β-naphthyl dienone, where both bicyclic ketone **34** and dinaphthylphenol **27** were formed, the identity of the product ratios can be interpreted as signifying the identity of the initial distribution of triplet excitation (i.e., at triplet "time zero") for the two modes of excited-state generation.

(17) (a) Zimmerman, H. E.; Keck, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3527–3528. (b) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5574–5581.

(18) (a) Barton, D. H. R.; DeMayo, P.; Shafiq, M. *Proc. Chem. Soc. London* **1957**, 205. (b) Barton, D. H. R.; DeMayo, P.; Shafiq, M. *J. Chem. Soc.* **1958**, 140–145. (c) Arigoni, D.; Bosshard, H.; Bruderer, H.; Buchi, G.; Jeger, O.; Krebaum, L. *Helv. Chim. Acta* **1957**, 929–935. (d) Schaffner, K.; Demuth, M. In "Rearrangements in Ground and Excited States"; Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 281–348.

(19) Zimmerman, H. E.; Hahn, R. C.; Morrison, H.; Wani, M. C. *J. Am. Chem. Soc.* **1965**, *87*, 1138–1140.

(20) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047.

(21) (a) Fisch and Richards (Fisch, M. H.; Richards, J. H. *J. Am. Chem. soc.* **1963**, *85*, 3029–3030) report a quantum yield of "approximately unity" for santonin. (b) Schuster and Patel (Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5154–5152) report a value of 0.75 for the type A photoreaction of 4-methyl-4-(trichloromethyl)cyclohexa-2,5-dien-1-one.

(22) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65–73.

Since the dioxetane entry to the triplet manifold has a dienone time zero locus of triplet excitation, we thus conclude that in the direct irradiation triplet excitation is engendered in the dienone chromophore. This is reasonable, since intersystem crossing at the carbonyl group should be enhanced by spin–orbit coupling,[12,23] and singlet energy transfer from the initially excited naphthyl group to the dienone chromophore is exothermic and should be rapid.[24d-f]

Less stringent evidence, nevertheless still in accord with this view of direct irradiation leading to triplet birth at the carbonyl group, is the observation that the dioxetane thermolysis and the direct irradiation product was the same also for the α-naphthyl dienone **1**.[25]

Hence, two of the three modes of triplet generation provide a triplet with excitation initially localized in the cyclohexadienone moiety.

The third mode of triplet generation was sensitization. Here product distributions contrasted with those of the dioxetane and direct irradiation approaches in the photochemistry of the β-naphthyl dienone **2**. The preferential excitation of the naphthyl moieties, as evidenced by formation of 96% dinaphthylphenol **27** and ca. 4% bicyclic ketone **34**, is of considerable interest.

Thus, the efficiency of transfer to naphthyl by either of the two sensitizers used would be perfectly efficient if only one acceptor site were available. Here the efficiency of transfer is given by eq 14.[3,16] Even in the most endothermic case at hand, namely

$$\phi_{sens} = \phi_r \left[\frac{1 + k_{ET}R\tau_s}{1 + k_{ET}R\tau_s + k_{-ET}S\tau_r} \right] \quad (14)$$

the transfer from thioxanthone triplet to dienone, using the known lifetimes,[26] the 3-kcal/mol endothermicity, and an assumed diffusion control for exothermic transfer, we predict a 0.99 efficient transfer to dienone. This efficiency derives from the very rapid rate of dienone type A rearrangement once dienone is excited.

However, with two acceptor sites available for energy transfer in the dinaphthyl dienones, selectivity is encountered wherein a

(23) (a) A value of k_{isc} of 10^6 s^{-1} is reported for naphthalene: Birks, J. B. "Organic Molecular Photophysics"; Wiley: New York, 1970; Vol. 2. (b) For benzophenone, a value of 10^{11} s^{-1} is reported: Dym, S.; Hochstrasser, R. M. *J. Chem. Phys.* **1969**, *51*, 2458–2468.

(24) (a) Even in rigid "rod-like molecules" and even at 7 Å distances singlet energy migration is known to be facile (e.g., 2.9×10^9 s^{-1} for the [1]-rod naphthyl to acetyl transfer). (b) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951. (c) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645. (d) One would anticipate a natural rate of fluorescence of the order of 10^7 s^{-1}. Thus energy transfer at a rate of the order of 10^9 s^{-1} would permit fluorescence as observed. However, naphthalenes are known[25e] to be quenched by 0.1 M cyclohexadiene at pseudounimolecular rates of the order of 10^7–10^9 s^{-1} depending on naphthalene substitution. Naphthalene itself is quenched at a rate of 2.5×10^9 L mol^{-1} s^{-1} [24f] or a rate of 2.5×10^8 s^{-1} in 0.1 M cyclohexadiene. Thus, the present lack of quenching suggests that the naphthylcyclohexadienones are quenched at a rate at the lower end of the rate, perhaps due to steric hindrance.[24e] (e) Labrianca, D. A.; Taylor, G. N.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3679–3683. (f) Stevenson, L. M.; Hammond, G. S. *Pure Appl. Chem.* **1968**, *16*, 125–136.

(25) The present dioxetane results do bear on our previous findings[17] dealing with the β-naphthylmethyldioxetane derived from 4,4-diphenylcyclohexadienone. Here a type A rearrangement, deriving from the 69 kcal/mol dienone triplet, occurred rather than formation of β-acetonaphthone triplet (E_T = 59 kcal/mol). This is somewhat parallel to the present observation of appreciable type A rearrangement from T_2 in competition with formation of T_1 by energy transfer to the naphthyl groups. With the present observations in hand, we suggest that in our diphenyl study, the partition of excitation energy may well be similarly controlled by a very rapid type A rearrangement competing with departure of an acetonaphthone triplet from a triplet pair.

(26) (a) The lifetimes used are those given in Table II except for thioxanthone[26b] (77 μs). (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769. (c) It may be that selective triplet transfer to the naphthyl groups results from a preference for $^3(n–\pi^*)$ to $^3(\pi–\pi^*)$ and $^3(n–\pi^*)$ to $^3(n–\pi^*)$ energy transfer as described by several authors.[26d-f] (d) Mirbach et al. (Mirbach, M. R.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471–474) report much slower rates of energy transfer for the $^3(n–\pi^*)$ to $^3(n–\pi^*)$ type due to localization of the excitation and poor overlap between donors and acceptors. (e) Saltiel et al. (Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799–6808) noted the localization of excitation in triplet acetone. (f) Note also: Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238.

Scheme IV. Rearrangements of the β-Naphthyl Dienone
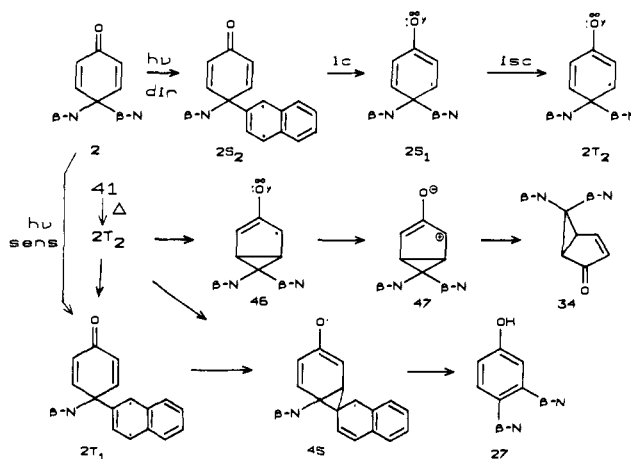
Scheme V. Rearrangements of the α-Naphthyl Dienone
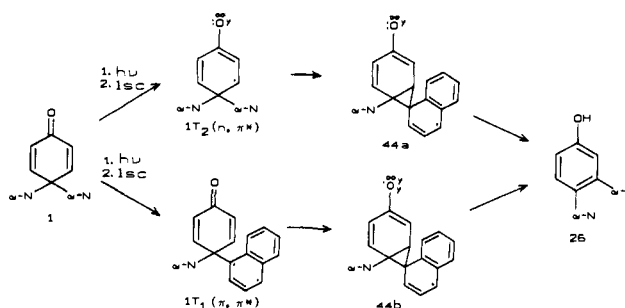
preferential transfer to the lowest energy chromophore occurs. Assuming steady-state kinetics, and energy transfer to both dienone and naphthyl chromophores, we readily obtain eq 15 which affords a ratio of quantum yields (ϕ_E and ϕ_X) originating from the enone and naphthyl excited species (E and X). Here the P's are the
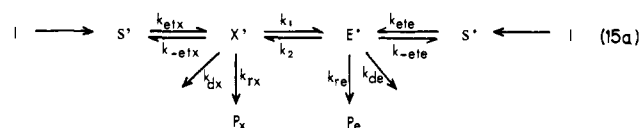
$$\phi_E/\phi_X = \left[\frac{(P_1 k_{ETX} + k_{ETE})K_X k_{rE}}{(P_2 k_{ETE} + k_{ETX})K_E k_{rX}} \right] \quad (15b)$$

where $P_1 = k_1/K_X$, $P_2 = k_2/K_E$, $K_X = (k_1 + k_{-ETX} + k_{rX} + k_{dX})$, and $K_E = (k_2 + k_{-ETE} + k_{rE} + k_{dE})$

probability of energy transfer from one chromophore to the other. The K's represent the sum of all rates available to each excited state. However, the main point here is that eq 15b does not necessarily afford unity but rather permits selectivity of chromophore excitation and reaction.[26c-f]

Molecular Aspects of the Rearrangements. Scheme IV depicts the course of the direct, thermally generated, and sensitized reactions. Scheme V outlines possible pathways for α-naphthyl migration. In this case it is not possible to determine with certainty what fraction of the reaction utilizes T_1 vs. T_2. It appears that the main source of different reactivity in the α- and β-naphthyl dienones **1** and **2** comes from the greater ability of the α-naphthyl group to bond at C-1 (i.e., α) compared with β bonding by the β-naphthyl moieties of dienone **2**. Where the naphthyl moieties are excited, this has precedent in the enhanced ability of triplet excited α-naphthyl chromophores to bond to vinyl sites compared with β-naphthyl triplets, as observed in naphthobarrelene photochemistry.[27] One way of understanding this selectivity is by

(27) (a) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1969**, *91*, 7516–7518. (b) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366–4376.

comparison of the α-bridged triplet diradical **44** with its β counterpart **45**. Independent of the electronic configuration, the α-bridged species has greater electron delocalization in precise analogy with the ground-state σ intermediates of naphthalene substitution chemistry. An alternative factor may be the greater delocalization of excitation via transannular (naphthyl–enone) overlap, which could facilitate direct formation of T_1 in the α-naphthyl dienone.

The most exciting aspect of the observed photochemistry is the ability of naphthyl migration to compete with the ubiquitous type A rearrangement. In the case of the β-naphthyl dienone it is clear that this naphthyl migration arises not only from the π–π^* triplet but also to a small extent from the n–π^* triplet.

Thus, while α-naphthyl has a greater migration ability than β-naphthyl, the latter is still more able to migrate than phenyl which has often been the group at C-4 in dienones previously studied.

There is the interesting question regarding the nature of the bridged species **44** and **45**. One can envisage an n–π^* configuration, a π–π^* configuration, and a zwitterion. In our earlier studies, the very facile migration of both *p*-anisyl and *p*-cyanophenyl groups was interpreted as signifying that, during the migration process, a zwitterion was not involved.[20] However, after the rate-limiting portion of the rearrangement, internal conversion to the zwitterion would account for final formation of a ground-state product.

Conclusion. The present study describes a first clear example where selective transfer of energy to two different triplet levels of one molecule permits one to excite one or the other end of the molecule and then observe different photochemistry from each of two excited states.

Experimental Section[28]

4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one. The general procedure of Reich, Renga, and Reich[30] was used. To a −78 °C solution of 2.72 mmol of lithium diisopropyl amide, prepared by the addition of 1.81 mL (2.90 mmol) of 1.5 M *n*-butyllithium in hexane to 0.41 mL (2.90 mmol) of diisopropylamine in 5 mL of THF at −78 °C, was added dropwise a solution of 0.776 g (2.22 mmol) of 4,4-di(α-naphthyl)cyclohex-2-en-1-one[2] in 15 mL of THF. The solution was allowed to stir at −78 °C for 1.5 h, then 0.418 g (1.33 mmol) of diphenyldiselenide was placed in the addition funnel, followed by 1 mL of THF and 0.073 mL (1.33 mmol) of bromine. The funnel was agitated and the contents added quickly to the anion solution. Acidic–basic workup of the cold solution gave the selenide as a yellow oil: NMR (270 MHz, CDCl$_3$) δ 6.70–8.15 (m, 15 H, arom and =CH), 6.21 (d, 1 H, J = 10.3 Hz, =CH), 4.27 (m, 1 H, –C*H*SePh), 3.48 (m, 1 H, –C*H*H–), 3.25 (m, 1 H, –CH*H*–).

To a 0 °C solution of 2.22 mmol of 4,4-di(α-naphthyl)-6-(phenylseleno)cyclohex-2-en-1-one in 7 mL of dichloromethane containing 0.36 mL of pyridine was added 0.60 mL (5.28 mmol) of 30% aqueous hy-

drogen peroxide. After the mixture was stirred at room temperature for 2 h, basic–acidic workup gave 0.834 g of a yellow oil which was crystallized with ether. Recrystallization from ether gave 0.456 g (59%) of the dienone as colorless needles, mp 208–210 °C.

The spectral data were the following: IR (KBr) 3080, 3040, 2960, 2860, 1665 (C=O), 1630, 1605, 1515, 1450, 1405, 1195, 1180, 1165, 1150, 1125, 855, 845, 820, 785, 750 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 6.98–7.86 (m, 15 H, arom and =CH), 6.41 (d, 1 H, J = 9.56 Hz, =CH); UV (CH$_3$CN) λ 250 (ϵ 23 200), 260 (14 700), 270 (17 300), 280 (21 300), 286 (21 500), 290 (20 800), 300 (14 000), 313 (5030), 325 (2860), 340 (490), tails to 350 nm; MS, *m/e* 346.1357 (calcd for C$_{26}$H$_{18}$O, *m/e* 346.13567).

Anal. Calcd for C$_{26}$H$_{18}$O: C, 90.14; H, 5.24. Found: C, 89.97; H, 5.31.

Exploratory Direct Photolysis of 4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 122 mg (0.325 mmol) of 4,4-di(α-naphthyl)-cyclohexa-2,5-dien-1-one in 250 mL of dry acetonitrile was purged with purified nitrogen[31] for 1 h prior to and during photolysis. The photolysis was performed on the "Wisconsin Black Box"[10] apparatus with the following filter cell combination: cell 1, 2.0 M nickel sulfate in 5% sulfuric acid; cell 2, 0.1 M copper sulfate in 5% sulfuric acid; cell 3, 0.1 M cobalt sulfate in 5% sulfuric acid. The transmission was 0% below 278 nm, 32.5% at 315 nm, and 0% above 348 nm.

The light output was measured by a digital electronic actinometer[32] calibrated by ferrioxalate actinometry[33] and indicated that the sample absorbed 0.202 mEinsteins of light.

The photolysate was concentrated in vacuo and subjected to preparative HPLC chromatography. Elution with 1:1 ether–dichloromethane gave fraction 1 [retention time 25.5 min, 51.6 mg (42%) of 3,4-di(α-naphthyl)phenol (mp 89–91 °C after recrystallization from ether)] and fraction 2 [retention time 29.3 min, 66.6 mg (55%) recovered dienone, pure by NMR].

The spectral data for 3,4-di(α-naphthyl)phenol were the following: IR (CHCl$_3$) 3580 (free -OH), 3300 (H-bonded –OH), 3040, 3030, 2960, 1605, 1600, 1590, 1570, 1505, 1490, 1425, 1390, 1300, 1275, 1255, 1220, 1180, 1165, 1110, 1020, 795, 775, cm^{-1}; NMR (270 MHz CDCl$_3$) δ 6.85–8.10 (m, 17 H, arom), 5.68 (s, 1 H, -OH); UV (CH$_3$CN) δ 240 (ϵ 13 000), 254 (5750), 272 (10 200), 283 (13 100), 292 (12 200), 300 (8410), 330 (1300), 348 (2430), 360 (1650), 380 (728), 347 (390), tails to 396 nm; MS, *m/e* 346.1357 (calcd for C$_{26}$H$_{18}$O, *m/e* 346.13567).

Anal. Calcd for C$_{26}$H$_{18}$O: C, 90.14; H, 5.24. Found: C, 90.04; H, 5.52.

Exploratory Sensitized Photolysis of 4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 59.0 mg (0.170 mmol) of 4,4-di(α-naphthyl)cyclohexa-2,5-dien-1-one and 252.7 mg of xanthone in 42 mL of dry acetonitrile was purged with purified nitrogen[31] for 1 h prior to and during photolysis. The photolysis was performed on the Microoptical bench[10] at 340 nm (22 nm half-width band-pass).

The light output was measured as described above and indicated that the sample absorbed 0.0636 mEinsteins of light.

The photolysate was concentrated in vacuo and subjected to preparative HPLC. Elution with 10% ether in dichloromethane gave fraction 1 [10.7 mg (18.2%) of 3,4-di(α-naphthyl)phenol], fraction 2 [250 mg of recovered xanthone], and fraction 3 [46.9 mg (76.9%) of recovered dienone].

Acid-Catalyzed Rearrangement of 4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 53 mg (0.150 mmol) of 4,4-di(α-naphthyl)-cyclohexa-2,5-dien-1-one in 20 mL of glacial acetic acid and 10 mL of distilled water was heated at 80 °C for 3 min and cooled to room temperature. Basic–acidic workup gave 69 mg of a yellow oil which was crystallized with ether to give 47 mg (89%) of 3,4-di(α-naphthyl)phenol as colorless needles.

The spectral data were identical with the data for the material obtained via photolysis of the dienone.

Summary of Quantum Yield Results for 4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one. All direct, sensitized, and quenched quantum yield determinations were performed with use of the microoptical bench employing a Bausch and Lomb 33-86-79 Monochromator having a 5.4-mm entrance slit and a 3.0-mm exit slit and an Osram HBO 200-W high-pressure mercury lamp. Light output was measured as described above.

Analysis was by HPLC eluting with 10% ether in dichloromethane and with a flow rate of 2.1 mL/min. The internal standard was purified naphthalene.

All direct and sensitized runs were purged with purified nitrogen[31] for

(28) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN 37921. All reactions were run under a dry nitrogen atmosphere unless otherwise stated. Anhydrous sodium sulfate or magnesium sulfate were used as drying agents. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector and an LDC 6000-psi minipump. Analyses were performed with a 0.95 × 50 cm polished stainless steel column packed with 5–15 μm porous silica beads. Preparative separations were performed with a 0.95 × 64 cm column packed with 10–20 μm porous silica beads.[29] Neutral workup refers to diluting with ether, washing with water and brine, drying, filtering, and concentrating in vacuo. Acidic workup added an initial 5% HCl wash after dilution. Basic workup added an initial saturated Na$_2$CO$_3$ wash after dilution. Basic–acidic workup used acid and base washes after dilution. Acetonitrile used for irradiation experiments was distilled from calcium hydride before use. Tetrahydrofuran (THF) was purified by storage over potassium hydroxide, followed by successive distillation under a nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Dichloromethane was purified by distillation from phosphorus pentoxide.

(29) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K., unpublished results.

(30) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.

(31) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

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Table III. Summary of Quantum Yield Data for 4,4-Di(α-naphthyl)cyclohexa-2,5-dien-1-one[a]

run	additive[b]	wavelength, nm	mmol of product ($\times 10^3$)	mEinsteins absorbed ($\times 10^3$)	% conv	ϕ phenol
1	none	313	4.752	4.605	5.02	1.031
2	none	313	1.683	1.752	2.80	0.961
3	none	313	0.915	0.898	1.03	1.018
4	X	340	2.242	3.817	2.94	0.589
5	X	340	1.564	1.934	2.01	0.814
6	X	340	0.635	0.775	0.82	0.820
7	X	340	0.392	0.404	0.49	0.970
8	0.19 M C	313	0.412	0.667	0.50	0.619
9	0.15 M C	313	0.387	0.551	0.50	0.687
10	0.05 M C	313	0.540	0.627	0.79	0.862

[a] Photolyses conducted in acetonitrile. [b] C = 1,3-cyclohexadiene, X = 1.27×10^{-2} M xanthone.

1 h prior to and during photolysis. For quenched quantum yield runs, samples were purged for 1 h prior to addition of quencher and were not purged during photolysis due to the volatility of 1,3-cyclohexadiene. All runs are summarized in Table III. The quenching study resulted in a straight-line Stern-Volmer plot with a slope of 3.08 M^{-1}.

Ethyl 2-Carboethoxy-3,4-di(α-naphthyl)-5-oxohexanoate. To a stirred solution of 0.75 g (5.43 mmol) of potassium *tert*-butoxide in 10 mL of THF at 0 °C was added dropwise a solution of 1.0 g (5.43 mmol) of 1-naphthylacetone in 10 mL of THF. After the mixture was stirred for 10 min, a solution of 1.62 g (95.4 mmol) of diethyl 1-naphthylidene malonate[34] in 20 mL of THF was added dropwise. The mixture was allowed to stir at 0 °C for an additional 30 min, and at room temperature for 12 h, then acidic workup gave 1.121 g of a yellow foam which was crystallized from ether to give 0.694 g (34%) of product as a white crystalline solid, mp 178–179 °C.

The spectral data were the following: IR (KBr) 3440, 3090, 3040, 2960, 2910, 2880, 1750, 1710, 1595, 1505, 1472, 1455, 1445, 1440, 1395, 1385, 1365, 1350, 1340, 1305, 1270, 1250, 1230, 1225, 1210, 1175, 1155, 1150, 1115, 1095, 1095, 1075, 1070, 1030, 978, 950, 865, 855, 800, 790, 720, 733, 710 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 8.40 (m, 2 H, naphthyl peri H), 7.24–7.70 (m, 10 H, naphthyl), 6.85–7.19 (m, 2 H, naphthyl), 5.58–5.76 (m, 2 H, C2-CH and C4-CH), 3.92–4.16 (m, 5 H, -CH$_2$-, -CH$_2$-, and C3-CH), 2.07 (s, 3 H, -CH$_3$), 1.15 (t, 3 H, J = 7.08 Hz, -CH$_3$), 0.99 (t, 3 H, J = 7.08 Hz, -CH$_3$); MS, m/e 482.2093 (calcd for C$_{31}$H$_{30}$O$_5$, m/e 482.20915).

Anal. Calcd for C$_{31}$H$_{30}$O$_5$: C, 77.16; H, 6.27. Found: C, 77.24; H, 6.43.

3,4-Di(α-naphthyl)-5-oxohexanoic Acid. A mixture of 0.106 g (0.218 mmol) of ethyl 2-carboxy-3,4-di(α-naphthyl)-5-oxohexanoate, 10 mL of glacial acetic acid, 5 mL of concentrated hydrochloric acid, and 6 mL of water was heated at reflux for 18 h, cooled, and concentrated in vacuo. Neutral workup of the residue gave 85 mg of a green-brown solid which was decolorized with Norite and recrystallized from dichloromethane-hexane to give 36 mg (43%) of the desired product as a colorless crystalline solid, mp 210–212 °C.

The spectral data were the following: IR (KBr) 2400–3400 (br -OH), 3040, 3020, 2995, 2940, 2880, 1700, 1580, 1505, 1430, 1410, 1390, 1345, 1305, 1260, 1220, 1170, 1150, 1080, 1025, 950, 860, 760, 730 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 7.0–8.5 (m, 14 H, naphthyl), 5.0–5.3 (m, 2 H, C4-CH and C5-CH), 3.1 (d, 2 H, J = 6.8 Hz, -CH$_2$-), 1.8 (s, 3 H, -CH$_3$); MS, m/e 382.1571 (calcd for C$_{26}$H$_{22}$O$_3$, m/e 382.12677).

Anal. Calcd for C$_{26}$H$_{22}$O$_3$: C, 81.65; H, 5.80. Found: C, 81.83; H, 5.93.

Methyl 3,4-Di(α-naphthyl)-5-oxohexanoate. A solution of 0.202 g (0.528 mmol) of 3,4-di(α-naphthyl)-5-oxohexanoic acid in 20 mL of methanol containing 0.1 mL of sulfuric acid was heated at reflux for 17 h, cooled, and poured into ice water; neutral workup gave 0.210 g of a yellow oil which was crystallized from ether-pentane to give 0.162 g (78%) of methyl 3,4-di(α-naphthyl)-5-oxohexanoate as a crystalline solid, mp 137–139 °C.

The spectral data were the following: IR (KBr) 3015, 3010, 2940, 2900, 1730, 1592, 1508, 1435, 1395, 1350, 1150, 800, 778, cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.0–8.6 (m, 14 H, arom), 5.0–5.4 (m, 2 H, 2 -CH), 3.5 (s, 3 H, -OCH$_3$), 3.1 (m, 2 H, -CH$_2$), 2.1 (s, 3 H, -CH$_3$); MS, m/e 396.1725 (calcd for C$_{27}$H$_{24}$O$_2$, m/e 396.17241).

Anal. Calcd for C$_{27}$H$_{24}$O$_2$: C, 81.79; H, 6.10. Found: C, 81.57; H, 6.17.

4,5-Di(α-naphthyl)cyclohexa-1,3-dione. To a stirred solution of 0.230 g (0.579 mmol) of methyl 3,4-di(α-naphthyl)-5-oxohexanoate in 15 mL of methanol at room temperature was added 0.16 mL (0.695 mmol) of 4.38 M sodium methoxide in methanol. After being at reflux for 12 h,

the solution was cooled to room temperature and acidic workup gave 0.186 g of a yellow foam which was chromatographed on a 2 × 24 cm hexane slurry packed silica gel column eluted with 50 mL of hexane, 700 mL of 50% ether-hexane, and 1500 mL of ether, collecting 50-mL fractions to give fractions 2–15 [32.0 mg of unidentified oil] and 16–45 [66 mg (31%) of 4,5-di(α-naphthyl)cyclohexa-1,3-dione as a white solid, mp 137–140 °C]. Recrystallization from ether-hexane gave 37 mg (18%) of dione, mp 144–145 °C.

The spectral data were the following: IR (KBr) 2400–3200 (br), 3010, 2900, 2625, 1750, 1400, 1192, 1105, 798, 775 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 9.20 (br s, 1 H, -OH), 7.05–8.00 (m, 14 H, naphthyl), 5.90 (s, 1 H, =CH), 4.48–4.90 (m, 2 H, 2 -CH), 2.82 (d, 1 H, J = 20.4 Hz, -CHH-), 2.64 (dd 1 H, J = 20.4, 7.3 Hz, -CHH-); MS, m/e 364.1462 (calcd for C$_{26}$H$_{20}$O$_2$, m/e 364.14622).

Anal. Calcd. for C$_{26}$H$_{20}$O$_2$: C, 85.69; H, 5.53. Found: C, 85.74; H, 5.65.

4,5-Di(α-naphthyl)-3-methoxycyclohex-2-en-1-one and 5,6-Di(α-naphthyl)-3-methoxycyclohex-2-en-1-one. A solution of 1.05 g (2.88 mmol) of 4,5-di(α-naphthyl)cyclohexane-1,3-dione and 36 mg of p-toluenesulfonic acid in 1 L of benzene containing 100 mL of methanol was refluxed for 10 h, cooled, and concentrated in vacuo to give 1.084 g of a yellow foam. Preparative HPLC eluting with 10% ether in dichloromethane gave fraction 1 [retention time 11.5 min, 0.402 g (36.9%) of 5,6-di(α-naphthyl)-3-methoxycyclohex-2-en-1-one] and fraction 2 [retention time 21.6 min, 0.344 g (31.5%) of 4,5-di(α-naphthyl)-3-methoxycyclohex-2-en-1-one].

Recrystallization of fraction 1 from ether-hexane gave 0.328 g (30.1%) of 5,6-di(α-naphthyl)-3-methoxycyclohex-2-en-1-one as colorless crystals, mp 175–176 °C.

The spectral data were the following: IR (CCl$_4$) 3040, 3000, 2920, 2840, 1660 (C=O), 1620, 1510, 1460, 1440, 1400, 1380, 1370, 1335, 1315, 1230, 1200, 1180, 1175, 1160, 1130, 1025, 1005 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.10–8.00 (m, 14 H, naphthyl), 5.80 (s, 1 H, =CH), 4.76 (m, 2 H, 2 -CH), 3.80 (s, 3 H, -OCH$_3$), 2.96 (dd, 1 H, J = 16.9, 6.1 Hz, -CHH-), 2.80 (dd, 1 H, J = 16.9, 7.4 Hz, -CHH-); MS, m/e 378.1618 (calcd for C$_{27}$H$_{22}$O$_2$, m/e 378.16186).

Anal. Calcd for C$_{27}$H$_{22}$O$_2$: C, 85.69; H, 5.86. Found: C, 85.70; H, 6.00.

Recrystallization of fraction 2 from ether-hexane gave 0.295 g (27.1%) of 4,5-di(α-naphthyl)-3-methoxycyclohex-2-en-1-one as colorless crystals, mp 180–182 °C.

The spectral data were the following: IR (KBr) 3040, 3000, 2930, 1640 (C=O), 1580, 1510, 1460, 1440, 1400, 1350, 1275, 1220, 1180, 1085, 1020, 992, 845, 812, 800, 780 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.20–8.00 (m, 14 H, naphthyl), 5.90 (s, 1 H, =CH), 4.95 (br s, 1 H, -CH), 4.50 (br s, 1 H, -CH), 3.85 (s, 3 H, -OCH$_3$), 2.95 (dd, 1 H, J = 16.9, 6.75 Hz, -CHH-), 2.85 (dd, 1 H, J = 16.9, 5.4 Hz, -CHH-); MS m/e 378.1618 (calcd for C$_{27}$H$_{22}$O$_2$, m/e 378.16186).

Anal. Calcd for C$_{27}$H$_{22}$O$_2$: C, 85.69; H, 5.86. Found: C, 85.48; H, 5.95.

4,5-Di(α-naphthyl)cyclohex-2-en-1-one. To a suspension of 13 mg (0.33 mmol) of lithium aluminum hydride in 2.0 mL of THF was added a solution of 100 mg (0.264 mmol) of 5,6-di(α-naphthyl)-3-methoxy-cyclohex-2-en-1-one in 3.0 mL of THF. The mixture was stirred at reflux for 1 h, cooled to 0 °C, cautiously quenched with 10% sulfuric acid, and ether extracted. Neutral workup gave 99.5 mg of a clear oil. The oil was crystallized from ether-hexane to give 70.9 mg (77.1%) of a yellow solid, mp 160–169 °C, which was recrystallized from ether-pentane to give 25.3 mg (27.7%) of 4,5-di(α-naphthyl)cyclohex-2-en-1-one, mp 188–190 °C.

The spectral data were the following: IR (KBr) 3060, 3040, 3000, 2940, 1675 (C=O), 1600, 1515, 1400, 1390, 1280, 1265, 1240, 1155, 1035, 970, 860, 805, 800, 780 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.26–7.97 (m, 15 H, naphthyl and =CH), 6.37 (dd, 1 H, J = 10.0, 2.5 Hz, =CH), 4.95–5.03 (m, 1 H, -CH), 4.70 (m, 1 H, -CH), 2.94–3.00

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(m, 2 H, -CH₂); MS, *m/e* 348.1514 (calcd for C₂₆H₂₀O, *m/e* 348.15131).

Anal. Calcd for C₂₆H₂₀O: C, 89.62; H, 5.79. Found: C, 89.96; H, 6.15.

5,6-Di(α-naphthyl)cyclohex-2-en-1-one. To a stirred suspension of 13 mg (0.33 mmol) of lithium aluminum hydride in 2.0 mL of THF was added a solution of 100 mg (0.264 mmol) of 4,5-di(α-naphthyl)-3-methoxycyclohex-2-en-1-one in 3 mL of THF. The mixture was stirred at reflux for 1 h, cooled to 0 °C, cautiously quenched with 10% sulfuric acid, and ether extracted. Neutral workup gave 94.3 mg of a clear oil which was crystallized from ether-hexane to give 65.9 mg (66.0%) of product, mp 162–164 °C.

The spectral data were the following: IR (KBr) 3060, 3040, 2990, 2910, 1690 (C=O), 1600, 1515, 1510, 1430, 1400, 1390, 1295, 1265, 1235, 1200, 1150, 1090, 1040, 930, 915 cm⁻¹; NMR (200 MHz, CDCl₃) δ 7.02–8.00 (m, 15 H, naphthyl and =CH), 6.42 (d, 1 H, *J* = 10.0 Hz, =CH), 4.95 (d, 1 H, *J* = 10.0 Hz, C5-CH), 4.88 (m, 1 H, C5-CH), 2.95 (dt, 1 H, *J* = 17.5, 4.5 Hz, -C*H*H-), 2.74 (dd, 1 H, *J* = 17.5, 10.0 Hz, -CH*H*-); MS *m/e* 348.1527 (calcd for C₂₆H₂₀O, *m/e* 348.15131).

Anal. Calcd for C₂₆H₂₀O: C, 89.62; H, 5.79. Found: C, 89.49; H, 6.04.

3,4-Di(α-naphthyl)phenol. A solution of 50.0 mg (0.144 mmol) of a mixture of 4,5-di(α-naphthyl)cyclohex-2-en-1-one and 4,5-di(α-naphthyl)cyclohex-3-en-1-one and 44.0 mg (0.194 mmol) of dicyanodichlorobenzoquinone in 2 mL of dry dioxane was refluxed 24 h, cooled, filtered through Celite, and concentrated in vacuo to give a dark brown oil which was chromatographed on a 5 × 20 cm silica gel preparative thick layer plate eluted with 10% ether in hexane to give 40.0 mg (80.2%) of a white solid. Recrystallization from ether gave pure phenol.

The spectral data were identical with the data for the phenol obtained upon photolysis of the α-dienone.

2,3-Di(α-naphthyl)phenol. A solution of 50.0 mg (0.144 mmol) of a mixture of 5,6-di(α-naphthyl)cyclohex-2-en-1-one and 44.0 mg (0.194 mmol) of dicyanodichlorobenzoquinone in 2 mL of dry dioxane was refluxed 24 h, cooled, filtered through Celite, and concentrated in vacuo to give a dark brown oil which was chromatographed on a 5 × 20 cm silica gel preparative thick layer plate eluted with 10% ether in hexane to give 39.4 mg (79.2%) of a white solid. Recrystallization from ether gave pure phenol, mp 186–188 °C.

The spectral data were the following: IR (CCl₄) 3530 (free -OH), 3300 (br, H-bonded -OH), 3055, 2990, 2910, 2830, 1605, 1590, 1575, 1510, 1450, 1395, 1300, 1275, 1175, 1160, 1130, 1120, 1020, 970, 915, 905, 875, 865, 800 cm⁻¹; NMR (200 MHz, CDCl₃) δ 6.85–8.00 (m, 17 H, arom), 5.92 (s, 1 H, -OH); MS *m/e* 346.1407 (calcd for C₂₆H₁₈O, *m/e* 346.13567).

Anal. Calcd for C₂₆H₁₈O: C, 90.14; H, 5.24. Found: C, 90.25; H, 5.30.

4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. The general procedure of Reich, Renga, and Reich[30] was used. To a -78 °C solution of 4.74 mmol of lithium diisopropylamide prepared by the addition of 3.16 mL (4.74 mmol) of 1.5 M *n*-butyllithium in hexane to 0.95 mL (6.23 mmol) of diisopropylamine in 15 mL of THF at -78 °C was added dropwise a solution of 1.799 g (5.19 mmol) of 4,4-di(β-naphthyl)cyclohex-2-en-1-one[2] in 20 mL of THF. After the mixture was stirred for 30 min, 0.976 g (3.12 mmol) of diphenyl diselenide was placed in the addition funnel, followed by 2 mL of THF and 0.17 mL (3.12 mmol) of bromine. The funnel was agitated briefly, and the contents added quickly to the anion solution. The solution was warmed to 0 °C, and 3.12 mL of distilled water, 0.63 mL of glacial acetic acid, and 2.6 mL of 30% aqueous hydrogen peroxide were added. After the mixture was stirred at room temperature for 3 h, it was diluted with ether and the layers separated. Basic–acidic workup gave 1.827 g of a brown oil. Preparative HPLC eluting with 2% ether in dichloromethane gave 0.657 g (36.5%) of 4,4-di(β-naphthyl)cyclohexa-2,5-dien-1-one as a white solid, mp 115–118 °C. Recrystallization from ether-hexane gave 0.494 g (27%), mp 123–124 °C.

The spectral data were the following: IR (KBr) 3035, 2980, 2940, 2910, 1660 (C=O), 1620, 1592, 1500, 1460, 1430, 1395, 1350, 1265, 1175, 1150, 1120, 1060, 925, 890, 858, 815 cm⁻¹; NMR (200 MHz, CDCl₃) δ 7.30–7.90 (m, 16 H, naphthyl and =CH), 6.55 (d, 2 H, *J* = 10.6 Hz, =CH); UV (CH₃CN) λ 267 (ε 17000), 280 (12400) 306 (1860), 313, (990), 320 (560), 324 (250), tails to 330 nm; MS, *m/e* 346.1357 (calcd for C₂₆H₁₈O, *m/e* 346.13567).

Anal. Calcd for C₂₆H₁₈O: C, 90.14; H, 5.24. Found: C, 89.88; H, 5.31.

Exploratory Direct Photolysis of 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 192 mg (0.554 mmol) of 4,4-di(β-naphthyl)cyclohexa-2,5-dien-1-one in 250 mL of acetonitrile containing 1% distilled water was purged with purified nitrogen[31] for 1 h prior to and during photolysis. The photolysis was performed on the "Wisconsin Black

Box"[10] apparatus with the filter cell combination described above.

The light output was measured as described above and indicated that the sample had absorbed 1.32 mEinsteins of light.

The photolysate was concentrated in vacuo and subjected to preparative HPLC. Elution with 1% ether in dichloromethane gave fraction 1 [retention time 21.5 min, 76.6 mg (39.9%) of 3,4-di(β-naphthyl)phenol] fraction 2 [retention time 27.7 min, 48.1 mg (25.1%) of 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-2-en-1-one], and fraction 3 [retention time 42.3 min, 59.9 mg (31.2%) of recovered dienone].

Fraction 1 was obtained as an oil which solidified on standing to give 3,4-di(β-naphthyl)phenol as a white solid, mp 59–61 °C.

The spectral data were the following: IR (KBr) 3300 (br, -OH), 1600, 1578, 1560, 1500, 1460, 1445, 1425, 1380, 1350, 1300, 1270, 1235, 1180, 1120, 895, 860, 750 cm⁻¹; NMR (200 MHz, CDCl₃) δ 7.00–7.90 (m, 17 H, arom) 5.80 (s, 1 H, -OH); UV (CH₃CN) λ 286 (ε 14 200), 300 (10 400), 313 (5930), 330 (1550), tails to 348 nm; MS, *m/e* 346.1356 (calcd for C₂₆H₁₈O, *m/e* 346.13567).

Anal. Calcd for C₂₆H₁₈O: C, 90.14; H, 5.24. Found: C, 90.37; H, 5.33.

Fraction 2 was recrystallized from ether–pentane to give 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one, mp 121–123 °C.

The spectral data were the following: IR (CCl₄) 3060, 3010, 2960, 2915, 2850, 1710, 1635, 1610, 1580, 1515, 1475, 1345, 1270, 1185, 1140, 1100, 1050, 1030, 965, 955, 910, 815, 831, 714 cm⁻¹; NMR (200 MHz, CDCl₃) δ 7.35–7.85 (m, 15 H, C4-=CH and naphthyl), 5.57 (dd, 1 H, *J* = 5.5, 0.92 Hz, C3-=CH), 3.50 (dd, 1 H, *J* = 4.82, 2.52 Hz, C5-cyclopropyl), 3.01 (dd, *J* = 4.82, 0.92 Hz, C1-cyclopropyl); UV (CH₃CN) λ 270 (ε 17 600), 290 (9050), 313 (1770), 320 (1120), 328 (960), 344 (420), 360 (350), 374 (95), tails to 384 nm.

Anal. Calcd for C₂₆H₁₈O: C, 90.14; H, 5.24. Found: C, 90.03; H, 5.42.

Exploratory Sensitized Photolysis of 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 104.5 mg (0.302 mmol) of 4,4-di(β-naphthyl)cyclohex-2,5-dien-1-one and 492.5 mg (2.51 mmol) of xanthone in 250 mL of dry acetonitrile was purged with purified nitrogen[31] for 1 h prior to and during photolysis. The photolysis was performed with the "Wisconsin Black Box"[10] and the filter cell combination described above.

The light output was measured as previously described and indicated that the sample had absorbed 0.166 mEinsteins of light.

The photolysate was concentrated in vacuo and xanthone was removed by passing the photolysate through a short silica gel column eluted with 20% ether in hexane to give 480.6 mg of recovered xanthone. The column was washed with ether, and the mixture obtained was concentrated and subjected to preparative HPLC. Elution with 2% ether in dichloromethane gave fraction 1 [30.0 mg (29%) of 3,4-di(β-naphthyl)phenol], fraction 2 [1.0 mg (1.2%) of 6,6-di(β-naphthyl)bicyclo[3.1.0]-hex-3-en-2-one], and fraction 3 [72.1 mg (68%) of recovered dienone].

Acid-Catalyzed Rearrangement of 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. A solution of 100.0 mg (0.104 mmol) of 4,4-di(α-naphthyl)cyclohexa-2,5-dien-1-one in 2 mL of glacial acetic acid and 0.02 mL of distilled water and 0.02 mL of concentrated hydrochloric acid was heated at reflux for 5 h, cooled, and ether extracted. Basic–acidic workup gave 102.6 mg of a yellow oil which was subjected to preparative HPLC to give 71.6 mg (72%) of 3,4-di(α-naphthyl)phenol as a clear oil which solidified on standing.

The spectral data were identical with the data for the material obtained via photolysis of the β-dienone.

Summary of Quantum Yield Data for 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. Quantum yields were determined as previously described for the α-naphthyl case except that HPLC analysis was performed with 2% ether in dichloromethane as the eluting solvent.

The data are summarized in Table IV (vide infra). Stern–Volmer analysis of the quenching data for 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one gave a slope of 1.22 M⁻¹. The data for 3,4-di(β-naphthyl)-phenol gave a curved plot with an initial slope of 808 M⁻¹, a final slope of 35.11 M⁻¹, and an intercept of 27.35.

4-Di(β-naphthyl)methoxy-6,6-di(β-naphthyl)bicyclo[3,1,0]hex-3-en-2-one. To a stirred solution of 0.100 g (1.04 mmol) of cyclopenten-1,4-dione in 5 mL of dry benzene was added dropwise a solution of 2.08 mmol of di(2-naphthyl)diazomethane (prepared by stirring 0.616 g (2.08 mmol) of di(2-naphthyl) ketone hydrazone[35] with 2.1 g of yellow mercuric oxide in 5 mL of dry benzene for 24 h and filtration through Celite) in 15 mL of dry benzene. After the mixture was stirred for 48 h at room temperature, the solvent was removed in vacuo to give 0.737 g of a yellow foam which was chromatographed on a 2 × 20 cm hexane slurry packed silica gel column with 1200 mL of 20% ether in hexane collecting 100-mL fractions to give the desired product as a yellow solid from fractions 9–12.

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Table IV. Summary of Quantum Yield Data for 4,4-Di-(β-naphthyl)cyclohexa-2,5-dien-1-one[a]

run	additive[b]	mEinsteins abs ($\times 10^3$)	% conv	mmol of phenol ($\times 10^3$)	mmol of bicyclic	ϕ phenol	ϕ bicyclic
1	none	4.53	4.80	2.77	1.25	0.611	0.276
2	none	2.27	2.50	1.41	0.747	0.621	0.329
3	none	0.887	0.95	0.515	0.316	0.581	0.356
4	X	14.6	17.6	12.3	0.490	0.856	0.034
5	X	3.45	4.22	3.18	0.152	0.922	0.044
6	X	1.39	1.70	1.31	0.058	0.941	0.042
7	T	18.4	21.7	16.0	0.515	0.870	0.023
8	T	9.75	10.7	8.77	0.322	0.899	0.033
9	T	2.39	2.90	2.28	0.103	0.956	0.043
10	0.001 C	4.85	3.86	1.29	1.033	0.2660	0.213
11	0.005 C	4.81	3.52	0.529	1.049	0.1100	0.218
12	0.01 C	4.94	3.18	0.332	1.057	0.0671	0.214
13	0.02 C	5.22	2.32	0.141	0.8717	0.0270	0.167
14	0.03 C	4.80	2.67	0.126	1.008	0.0263	0.210
15	0.04 C	4.75	2.69	0.114	1.045	0.0239	0.220
16	0.05 C	6.36	3.25	0.136	1.520	0.0214	0.239
17	0.10 C	6.86	2.54	0.132	1.125	0.0192	0.164
18	0.20 C	6.10	2.89	0.109	0.9028	0.0179	0.148

[a] All runs in acetonitrile at 313 nm, except runs 7–9 at 334 nm. [b] X = 1.29×10^{-2} M xanthone, T = 1.62×10^{-2} M thioxanthone, C = 1,3-cyclohexadiene.

Recrystallization from ether–hexane gave 94 mg (7%) of bicyclic enone as colorless needles, mp 197–199 °C.

The spectral data were the following: IR (KBr) 3050, 3010, 2910, 1680 (C=O), 1570, 1510, 1500, 1370, 1355, 1325, 1270, 1225, 1185, 1120, 990, 860, 825, 795, 750 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 7.30–8.15 (m, 28 H, naphthyl), 6.02 (s, 1 H, =CH), 4.66 (s, 1 H, –CH), 3.46 (d, 1 H, J = 5.3 Hz, cyclopropyl), 2.89 (d, 1 H, J = 5.3 Hz, cyclopropyl); MS, m/e 628.2404 (calcd for C$_{47}$H$_{32}$O$_2$, m/e 628.24006).

Anal. Calcd for C$_{47}$H$_{32}$O$_2$: C, 89.78; H, 5.13. Found: C, 89.46; H, 5.21.

6,6-Di(β-naphthyl)-4-methoxybicyclo[3,1,0]hex-3-en-2-one. A mixture of 0.490 g (0.780 mmol) of 4-di(β-naphthyl)methoxy-6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one and 1 mg of *p*-toluenesulfonic acid in 25 mL of methanol was heated at reflux for 24 h, cooled, and concentrated in vacuo. The residue was chromatographed on a 2 × 30 cm hexane slurry packed silica gel column eluted with 20% ether in hexane and collecting 100-mL fractions to give 0.188 g (66.7%) of bicyclic enone as fractions 8–10, as a white foam, mp 67–69 °C.

The spectral data were the following: IR (KBr) 3050, 2970, 2930, 2840, 1685 (C=O), 1590, 1505, 1440, 1365, 1270, 1248, 1170, 1000, 950, 938, 910, 860, 825, 790, 750, 740, 700 cm^{-1}; NMR (270 MHz CDCl$_3$) δ 7.35–8.10 (m, 14 H, naphthyl), 4.56 (s, 1 H, =CH), 3.62 (s, 3 H, –OCH$_3$), 3.25 (d, 1 H, J = 5.6 Hz, C5-cyclopropyl), 3.09 (d, 1 H, J = 5.6 Hz, C1-cyclopropyl); MS, m/e 376.1463 (calcd for C$_{27}$H$_{20}$O$_2$, m/e 376.14622).

Anal. Calcd for C$_{27}$H$_{20}$O$_2$: C, 86.14; H, 5.36. Found: C, 85.86; H, 5.58.

endo-6,6-Di(β-naphthyl)-4-hydroxybicyclo[3.1.0]hexan-2-one. To a stirred solution of 0.188 g (0.52 mmol) of 6,6-di(β-naphthyl)-4-methoxybicyclo[3.1.0]hex-3-en-2-one at −78 °C was added dropwise 0.80 mL (0.78 mmol) of 0.98 M diisobutyl aluminum hydride in hexane. After the mixture was stirred for 3 h at room temperature, a few drops of methanol were added, followed by 5% aqueous hydrochloric acid, and product was extracted with ether. The ether layer was stirred with 2 M hydrochloric acid at room temperature for 30 min, and the layers were separated. Neutral workup gave 0.146 g of a white solid, which was recrystallized from ether to give 0.056 g (31%) of product as colorless crystals, mp 199–201 °C.

The spectral data were the following: IR (KBr) 3420, 3060, 3020, 2920, 2880, 1710, 1660, 1645, 1605, 1508, 1405, 1395, 1360, 1345, 1210, 1155, 1140, 1135, 1095, 1090, 985, 970, 955, 910, 880, 870, 830, 825, 795, 717, 705 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 7.35–8.10 (m, 14 H, naphthyl), 4.95 (m, 1 H, –CHOH), 3.25 (t, 1 H, J = 5.5 Hz, C5-cyclopropyl), 2.85 (d, 1 H, J = 5.5 Hz, C1-cyclopropyl), 2.40 (dd, J = 17.5, 10.0 Hz, exo C3-C*H*H–), 2.15 (br s, 1 H, –OH), 1.45 (dd, 1 H, J = 17.5, 8.0 Hz, endo C3-CH*H*–); MS, m/e 364.1462 (calcd for C$_{26}$H$_{20}$O$_2$, m/e 364.14622).

Anal. Calcd for C$_{26}$H$_{20}$O$_2$: C, 85.69; H, 5.64. Found: C, 85.36; H, 5.64.

endo-6,6-Di(β-naphthyl)-4-hydroxybicyclo[3.1.0]hexan-2-one Methanesulfonate. To a stirred solution of 24 mg (0.066 mmol) of endo-6,6-di(β-naphthyl)-4-hydroxybicyclo[3.1.0]hexane-2-one in 1 mL of dry dichloromethane at 0 °C was added 14 μL (0.099 mmol) of triethylamine and 5.6 μL (0.073 mmol) of methanesulfonyl chloride. After the mixture was stirred for 1 h at 0 °C, acidic–basic workup gave 28.5 mg of a white

solid which was recrystallized from ether–hexane to give 20.9 mg (71.6%) of product as colorless crystals, mp 133–135 °C.

The spectral data were the following: IR (CCl$_4$) 3060, 3050, 2950, 2920, 2840, 1740, 1635, 1600, 1500, 1570, 1445, 1410, 1370, 1345, 1260, 1180, 1100, 1030, 960, 950, 920, 905, 895, 865, 705 cm^{-1}; NMR (270 MHz, CDCl$_3$) δ 7.30–8.2 (m, 14 H, naphthyl), 5.70 (m, 1 H, –CHOMs), 3.05 (s, 3 H, –CH$_3$) 3.50 (t, 1 H, J = 6.8 Hz, C5-cyclopropyl), 2.95 (d, 1 H, J = 6.8 Hz, C1-cyclopropyl), 2.52 (dd, 1 H, J = 18.9, 10.1 Hz, exo C3-C*H*H–), 1.65 (dd, 1 H, J = 18.9, 10.1 Hz, endo C3-CH*H*–).

Anal. Calcd for C$_{27}$H$_{22}$O$_4$S: C, 73.29; H, 5.01. Found: C, 73.47; H, 5.09.

6,6-Di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one. To a stirred solution of 14.9 mg (0.034 mmol) of endo-6,6-di(β-naphthyl)-4-hydroxybicyclo-[3.1.0]hexane-2-one methanesulfonate in 2 mL of THF was added 4.5 mg (0.040 mmol) of potassium *tert*-butoxide. After the mixture was stirred at room temperature for 30 min, it was poured into water and ether extracted. Neutral workup gave 0.0158 g of a clear oil which was chromatographed on a 5 × 20 cm preparative thick layer silica gel plate and eluted with 20% ether in hexane to give 11.4 mg (96.8%) of product as a colorless oil which was crystallized from ether–pentane to give colorless needles, mp 121–123 °C.

The spectral data were identical with the data for the bicyclic obtained upon photolysis of the β-dienone.

4,5-Di(β-naphthyl)cyclohexane-1,3-dione. To a 0 °C solution of sodium ethoxide in ethanol, prepared by the addition of 3 mL of absolute ethanol to 0.16 g (6.96 mmol) of sodium, was added dropwise a solution of 1.11 g (5.51 mmol) of methyl 2-naphthylacetate in 10 mL of ethanol, followed by the addition of 1.01 g (5.14 mmol) of 2-naphthalacetone[36] in 15 mL of ethanol. The resulting mixture was warmed to room temperature over 1 h and then heated at reflux for 18 h. Water was added, and the resulting gummy precipitate was filtered through Celite. The filtrate was concentrated in vacuo, poured into 5% hydrochloric acid, and ether extracted. The ether extract was dried and concentrated to precipitate 1.39 g (85.5%) of a colorless crystalline product, mp 190–192 °C.

The spectral data were the following: IR (KBr) 2300–2600 (br –OH), 3045, 3010, 2960, 2900, 1580 (C=O), 1512, 1345, 1280, 1230, 1188, 1165, 860, 820, 785, 750 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 9.10 (br s, 1 H, –OH), 6.90–7.95 (m, 14 H, naphthyl), 5.80 (s, 1 H, =CH), 2.95 (m, 2 H, 2 –CH), 2.58 (m, 2 H, –CH$_2$); MS m/e 364.1462 (calcd for C$_{26}$H$_{20}$O$_2$, m/e 364.14622).

Anal. Calcd for C$_{26}$H$_{20}$O$_2$: C, 85.69; H, 5.53. Found: C, 85.46; H, 5.70.

4,5-Di(β-naphthyl)-3-methoxycyclohex-2-en-1-one and 5,6-Di(β-naphthyl)-3-methoxycyclohex-2-en-1-one. A solution of 139.4 mg (0.383 mmol) of 4,5-di(β-naphthyl)cyclohexane-1,3-dione and 5 mg of *p*-toluenesulfonic acid in 100 mL of benzene containing 10 mL of methanol was refluxed for 12 h, cooled, and concentrated in vacuo to give 131.9 mg of crude product which was subjected to preparative HPLC. Elution with 10% ether in dichloromethane gave fraction 1 [retention time 10.0 min, 52.2 mg (36.1%) of 5,6-di(β-naphthyl)-3-methoxycyclohex-2-en-1-

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(36) Wilds, A. L.; Beck, L. W.; Close, W. J.; Djerassi, C.; Johnson, J. A., Jr.; Johnson, T. L.; Shunk, C. H. *J. Am. Chem. Soc.* **1947**, *69*, 1985–1994.

one] and fraction 2 [retention time 21.9 min, 69.6 mg (48.1%) of 4,5-di(β-naphthyl)-3-methoxycyclohex-2-en-1-one].

Fraction 1 was recrystallized from ether–hexane to give 45.7 mg (31.6%) of 5,6-di(β-naphthyl)-3-methoxycyclohex-2-en-1-one as colorless crystals, mp 164–165 °C.

The spectral data were the following: IR (KBr) 3040, 2920, 2910, 1658 (C=O), 1620, 1512, 1465, 1445, 1430, 1385, 1375, 1305, 1275, 1220, 1205, 1170, 1160, 1000, 960, 920, 850 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.15–7.90 (m, 14 H, naphthyl), 5.70 (s, 1 H, =CH), 4.08 (d, 1 H, J = 12.2 Hz, C4-CH), 3.89 (ddd, 1 H, J = 18.9, 12.2, 5.4 Hz, C5-CH), 3.80 (s, 3 H, -OCH$_3$), 3.00 (dd, 1 H, J = 18.9, 12.2 Hz, -CHH-), 2.75 (dd, 1 H, J = 18.9, 5.4 Hz, -CHH-); MS, m/e 378.1620 (calcd for C$_{27}$H$_{22}$O$_2$, m/e 378.16186).

Anal. Calcd for C$_{27}$H$_{22}$O$_2$: C, 85.69; H, 5.86. Found: C, 85.73; H, 5.78.

Fraction 2 was recrystallized from ether–hexane to give 50.7 mg (35.0%) of 4,5-di(β-naphthyl)-3-methoxycyclohex-2-en-1-one as colorless crystals, mp 171–173 °C.

The spectral data were the following: IR (KBr) 3040, 3020, 2915, 1660 (C=O), 1625, 1510, 1450, 1430, 1380, 1375, 1215, 1170, 1150, 1010, 860 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.24–7.89 (m, 14 H, naphthyl), 5.78 (s, 1 H, =CH), 4.24 (d, 1 H, J = 6.8 Hz, -CH), 3.70 (m, 1 H, -CH), 3.68 (s, 3 H, -OCH$_3$), 2.90 (dd, 1 H, J = 20.3, 7.4 Hz, -CHH-), 2.80 (dd, 1 H, J = 20.3, 6.1 Hz, -CHH-); MS, m/e 378.1620 (calcd for C$_{27}$H$_{22}$O$_2$, m/e 378.16186).

Anal. Calcd for C$_{27}$H$_{22}$O$_2$: C, 85.69; H, 5.86. Found: C, 85.42; H, 5.94.

4,5-Di(β-naphthyl)cyclohex-2-en-1-one. To a stirred suspension of 36.3 mg (0.827 mmol) of lithium aluminum hydride in 7 mL of THF was added dropwise a solution of 250 mg (0.661 mmol) of 5,6-di(β-naphthyl)-3-methoxycyclohex-2-en-1-one in 15 mL of the THF. The mixture was heated at reflux for 2 h, cooled to 0 °C, and carefully quenched with 10% sulfuric acid. After the mixture was stirred at room temperature for an additional 2 h, ether was added and the layers were separated. Neutral workup gave 0.243 g of a slightly yellow foam which was crystallized with carbon tetrachloride–hexane to give 0.213 g (93%) of enone, mp 109–111 °C.

The spectral data were the following: IR (KBr) 3060, 3022, 2930, 1685 (C=O), 1610, 1510, 1400, 1395, 1385, 1285, 1140, 1065, 1030, 975, 960, 905, 868, 830, 755 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.05–7.90 (m, 15 H, arom and =CH), 6.35 (dd, 1 H, J = 10.0, 2.5 Hz, =CH), 4.25 (m, 1 H, -CH); 3.60 (m, 1 H, -CH), 2.80–3.40 (m, 2 H, -CH$_2$); MS, m/e 348.1514 (calcd for C$_{26}$H$_{20}$O, m/e 348.15131).

Anal. Calcd for C$_{26}$H$_{20}$O: C, 89.62; H, 5.79. Found^b C, 89.82; H, 5.47.

5,6-Di(β-naphthyl)cyclohex-2-en-1-one. To a stirred suspension of 21.8 mg (0.496 mmol) of lithium aluminum hydride in 4 mL of THF was added dropwise a solution of 150 mg (0.396 mmol) of 4,5-di(β-naphthyl)-3-methoxycyclohex-2-en-1-one in 10 mL of THF. The mixture was heated at reflux for 2 h, cooled to 0 °C, and carefully quenched with 10% sulfuric acid. After the mixture was stirred at room temperature for 2 h, ether was added, and the layers were separated. Neutral workup gave 0.138 g of a white solid which was recrystallized from ether–hexane to give 88 mg (69%) of pure enone, mp 136–138 °C.

The spectral data were the following: IR (KBr) 3050, 3015, 2910, 2895, 2850, 2820, 1680 (C=O), 1600, 1510, 1425, 1390, 1370, 1295, 1275, 1250, 1230, 1210, 1200, 1160, 1150, 1130, 950, 930, 900, 845, 820, 780, 750, 720, 665 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.10–7.75 (m, 15 H, naphthyl and =CH), 6.30 (dd, 1 H, J = 10.2, 2.4 Hz, =CH), 4.20 (d, 1 H, J = 12.4 Hz, -CH), 3.85–3.99 (m, 1 H, -CH), 2.81–2.89 (m, 2 H, -CH$_2$); MS, m/e 348.1514 (calcd for C$_{26}$H$_{20}$O, m/e 348.15131).

Anal. Calcd for C$_{26}$H$_{20}$O: C, 89.62; H, 5.79. Found: C, 89.53; H, 5.83.

3,4-Di(β-naphthyl)phenol. A mixture of 100 mg (0.287 mmol) of 4,5-di(β-naphthyl)cyclohex-2-en-1-one and 87.3 mg (0.387 mmol) of dicyanodichlorobenzoquinone in 2.5 mL of dry dioxane was heated at reflux for 24 h, cooled, and filtered through Celite to give 130 mg of a dark brown oil which was chromatographed on a 20 × 20 cm silica gel preparative thick layer plate eluted with 30% ether in hexane to give 26.8 mg (27%) of phenol as a white solid.

The spectral data were identical with those of the phenol obtained upon photolysis of the β-dienone.

2,3-Di(β-naphthyl)phenol. A mixture of 80.2 mg (0.230 mmol) of 5,6-di(β-naphthyl)cyclohex-2-en-1-one and 70.0 mg (0.310 mmol) of dicyanodichlorobenzoquinone in 2 mL of dry dioxane was refluxed for 24 h, cooled, filtered through Celite, and concentrated to give 110 mg of a dark brown oil which was chromatographed on a 20 × 20 cm silica gel preparative thick layer plate eluted with 30% ether in hexane to give 33 mg of the phenol as a yellow semisolid. Recrystallization from pentane gave 16 mg (20%) of colorless needles, mp 124–125 °C.

The spectral data were the following: IR (KBr) 3540 (free -OH),

3200, (br, H-bonded -OH), 3050, 3030, 2975, 2920, 1612, 1605, 1582, 1575, 1510, 1465, 1455, 1435, 1302, 1280, 1205, 1188, 1165, 1135, 905, 865, 825, 685 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 6.90–7.75 (m, 17 H, arom), 5.18 (s, 1 H, -OH); MS, m/e 346.1357 (calcd for C$_{26}$H$_{18}$O, m/e 346.13567).

Emission Measurements. Phosphorescence and fluorescence measurements were made on an Aminco-Kiers spectrophosphorimeter equipped with a Hanovia 901C-1, 150-W Xenon arc lamp, modified with internal baffles to eliminate scatter and interfaced to a PDP 11/55 microcomputer. The fluorescence spectra were obtained at 295 K and the phosphorescence spectra were obtained at 77 K in a methylcyclohexane–isopentane (4:1) glass with samples beings thoroughly degassed immediately before measurements were made. Table V (vide infra) summarizes the data obtained for dienones; the excitation wavelength was 313 nm.

Attempted Fluorescence Quenching of 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. With use of the Aminco-Kiers described above, the relative integrated fluorescence intensity of degassed samples of the dienone containing aliquots of 1,3-cyclohexadiene was measured at 295 K. The excitation wavelength was 320 nm, and the emission was detected at 350 nm. Integrated intensities were determined over 15-s intervals, subtracting for background counts with slits closed. With use of 1,3-cyclohexadiene concentrations of 0.0 to 0.20 M, any decrease in the relative fluorescence intensity was close to experimental error. Note Table VI.

Fluorescence Quantum Yield. The Fluorescence Efficiency of 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one. This was determined by using anthracene and quaterphenyl as standards and comparing emission intensities at 325 nm with excitation at 313 nm.

1-Isopropylidene-4,4-di(α-naphthyl)-2,5-cyclohexadiene, To a slurry of 417.6 mg (0.927 mmol) of isopropyltriphenylphosphonium iodide in 15 mL of dry THF was added dropwise at 0 °C a solution of 336.8 mg (0.972 mmol) of 4,4-di(α-naphthyl)cyclohexa-2,5-dien-1-one in 7 mL of THF. After the mixture was stirred overnight at room temperature, it was concentrated in vacuo and passed through a 3.5 × 30 cm silica gel column slurry packed with hexane and eluted with hexane to give 0.328 g (91%) of a yellow solid which was recrystallized from methanol to give colorless needles, mp 142–144 °C.

The spectral data were the following: IR (KBr) 3025, 3000, 2900, 2940, 1590, 1565, 1500, 1430, 1388, 1372, 1335, 1260, 1240, 1225, 1155, 1075, 942, 910, 790, 765 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 6.85–7.95 (m, 14 H, naphthyl), 6.50 (d, 2 H, J = 12.5 Hz, =CH), 6.42 (d, 2 H, J = 12.5 Hz, =CH), 1.70 (s, 6 H, -CH$_3$); MS , m/e 372.1877 (calcd for C$_{29}$H$_{24}$, m/e 372.18768).

Anal. Calcd for C$_{29}$H$_{24}$: C, 93.50; H, 6.50. Found: C, 93.57; H, 6.57.

1-Isopropylidene-4,4-di(β-naphthyl)-2,5-cyclohexadiene. To a slurry of 0.983 g (2.29 mmol) of isopropyltriphenylphosphonium iodide in 35 mL of THF was added dropwise at 0 °C 1.29 mL (2.29 mmol) of 1.5 M n-butyllithium in hexane. After the mixture was stirred for 1 h at room temperature, a solution of 0.793 g (2.29 mmol) of 4,4-di(β-naphthyl)cyclohexa-2,5-dien-1-one in 18 mL of THF was added dropwise and the mixture stirred overnight and then poured into hexane and cooled to 0 °C. The resulting precipitate was removed by filtration through Celite and the filtrate washed with saturated aqueous ammonium chloride and water, dried, and concentrated to give 0.269 g of a yellow oil. Crystallization with carbon tetrachloride–hexane gave 0.201 g (23.6%) colorless needles, mp 148–150 °C.

The spectral data were the following: IR (KBr) 3035, 3010, 2970, 2920, 2860, 1600, 1502, 1485, 1440, 1385, 1275, 1195, 1180, 1032, 1025, 1005, 948, 935, 900, 865, 820, 755, 725, 700 cm^{-1}; NMR (200 MHz, CDCl$_3$) δ 7.25–8.00 (m, 14 H, naphthyl), 6.80 (d, 2 H, J = 10.0 Hz, =CH), 6.20 (d, 2 H, J = 10.0 Hz, =CH), 1.70 (s, 6 H, -CH$_3$); MS m/e 372.1877 (calcd for C$_{29}$H$_{24}$, m/e 372.18768).

Anal. Calcd for C$_{29}$H$_{24}$: C, 93.50; H, 6.50. Found: C, 93.60; H, 6.54.

Photooxygenation of 1-Isopropylidene-4,4-di(α-naphthyl)-2,5-cyclohexadiene. A solution of 111 mg (0.298 mmol) of 1-isopropylidene-4,4-di(α-naphthyl)-2,5-cyclohexadiene and 5.5 mg (0.015 mmol) of methylene blue in 10 mL of 1:1 methanol–acetone was cooled to -60 °C and saturated with oxygen. Irradiation with a tungsten lamp with continuous oxygen bubbling for 4 h resulted in complete reaction by thin-layer analysis. Norite and ether were added, and the mixture was stirred at -78 °C for 30 min. Filtration through Celite and concentration in vacuo at -10 °C gave a clear oil which was crystallized with pentane–ether at -15 °C to give 39.1 mg (32%) of pure dioxetane, mp 104–106 °C.

NMR (200 MHz, CDCl$_3$) δ 6.90–7.95 (m, 14 H, naphthyl), 6.64 (d, 2 H, J = 10.0 Hz, =CH), 6.70 (d, 2 H, J = 10.0 Hz, =CH), 1.40 (s, 6 H, -CH$_3$).

Photooxygenation of 1-Isopropylidene-4,4-di(β-naphthyl)-2,5-cyclo-

Table V. Emission Measurements for 4,4-Di(α-naphthyl)- and 4,4-Di(β-naphthyl)cyclohexa-2,5-dien-1-one[a]

dienone	wavelgth 0–0 (f), nm	wavelgth 0–0 (p), nm	$E(s)$, kcal/ mol	$E(t)$, kcal/ mol	fluores- cence efficiency
α-naphthyl	weak	491.6		58.16	
β-naphthyl	325.3	486.5	87.90	58.77	0.026[b]
					0.020[c]

[a] f refers to fluorescence and p to phosphorescence. [b] Standard anthracene ($\phi_f = 0.36$[11a]) and excitation at 313 nm. [c] Standard quaterphenyl ($\phi_f = 0.89$[11a]) and excitation at 313 nm.

Table VI. Typical Attempted Fluorescence Quenching Results[a]

quencher concn	average intensity	I_0/I
none	0.290	1.000
0.05	0.290	1.000
0.10	0.295	0.983
0.15	0.277	1.048
0.20	0.272	1.067

[a] Enone concentration 0.00113 M.

hexadiene. A solution of 200 mg (0.536 mmol) of 1-isopropylidene-4,4-di(β-naphthyl)-2,5-cyclohexadiene and 10 mg of methylene blue in 20 mL of 1:1 methanol-acetone was cooled to –60 °C and saturated with oxygen. Irradiation with a tungsten lamp with continuous oxygen bubbling for 2.5 h resulted in complete reaction by thin-layer analysis. Norite and ether were added, and the mixture was stirred at –70 °C for 15 min and filtered through Celite. After concentration in vacuo at –10 °C, ether was added and product precipitated. The precipitate was recrystallized from ether at –15 °C to give 55.4 mg (25.6%) of pure dioxetane, mp 93–95 °C.

NMR (200 MHz, CDCl$_3$) δ 7.20–7.90 (m, 14 H, naphthyl), 6.68 (d, 2 H, J = 11.0 Hz, =CH), 6.70 (d, 2 H, J = 11.0 Hz, =CH), 1.55 (s, 6 H, -CH$_3$).

Thermolysis of 3,3-Dimethyl-7,7-di(α-naphthyl)-1,2-dioxaspiro[3.5]-nona-5,8-diene. A solution of 20.0 mg (0.050 mmol) of dioxetane in 50 mL of dry acetonitrile was heated at 82 °C for 18 h, cooled, and concentrated in vacuo to give 22 mg of a yellow oil. HPLC analysis of the mixture gave two products: 4,4-di(α-naphthyl)cyclohexa-2,5-dien-1-one and 3,4-di(α-naphthyl)phenol in a ratio of 79:21.

Thermolysis of 3,3-Dimethyl-7,7-di(β-naphthyl)-1,2-dioxaspiro[3.5]-nona-5,8-diene. A solution of 14.9 mg (0.037 mmol) of dioxetane in 50 mL of dry acetonitrile was heated at 82 °C for 8 h and concentrated in vacuo to give 15 mg of yellow oil. HPLC analysis of the mixture gave three products: 4,4-di(β-naphthyl)cyclohexa-2,5-dien-1-one, 6,6-di(β-naphthyl)bicyclo[3.1.0]hex-3-en-2-one, 3,4-di(β-naphthyl)phenol in a ratio of 94.9:3.2:2.0.

Appendix

Solution of Dual Slope Stern–Volmer Plot for Lifetimes. Assuming no conversion of the upper state to the lower one, we have eq 1, 2 and 3 from P. J. Wagner:[16a]

$$m_f = (1 + R)T_2$$
where $R = \phi_1/\phi_2$, $T_1 = k_{q1}\tau_1$, and $T_2 = k_{q2}\tau_2 \qquad (1)$

$$I = (1 + R)(1 - RT_2/T_1) \qquad (2)$$

$$m_i = T_2 + RT_1/(1 + R) \qquad (3)$$

From eq 1

$$R = (m_f - T_2)/T_2 \qquad (4)$$

From eq 2 and 4

$$I = m_f(T_1 + T_2 - m_f)/(T_1T_2) \qquad (5)$$

From eq 3 and 4

$$m_i = \frac{[m_f(T_1 + T_2) - T_1T_2]}{m_f} \qquad (6)$$

From eq 5

$$T_2 = m_f(T_1 - m_f)/(IT_1 - m_f) \qquad (7)$$

From eq 6

$$T_2 = m_f(m_i - T_1)/(m_f - T_1) \qquad (8)$$

From eq 7 and 8, eliminating T_2

$$(I - 1)T_1^2 - (Im_i - m_f)T_1 + m_im_f - m_f^2 = 0 \qquad (9)$$

Also from eq 7 and 8, eliminating T_1

$$(I - 1)T_2^2 - (Im_i - m_f)T_2 + m_im_f - m_f^2 = 0 \qquad (10)$$

The last two quadratic equations are seen to be identical in form. Thus the one quadratic provides both solutions to both T_1 and T_2

$$T_x = 1/2(I - 1)[(Im_i - m_f) \pm \text{root}], \text{ where } x = 1 \text{ or } 2 \qquad (11)$$

$$\text{where root} = (Im_i - m_f)^2 - 4(m_im_f - m_f^2)(I - 1)$$

Substituting for the definition of T_x we obtain

$$k_{qx} = 1/2(I - 1)[(Im_i - m_f) \pm \text{root}], \text{ where } x = 1 \text{ or } 2 \qquad (12)$$