

Elution was performed with 10% ethyl acetate-hexane, with *p*-methoxybenzophenone used as internal standard. Where relative amounts of products were very different, analyses for the major and minor components were carried out in separate injections, with the concentration of internal standard being adjusted to close to that of the component being analyzed. The resulting curves were integrated by PDP-11/55 digitization with a Bitpad (Summagraphics Co.) digitizer and appropriate programming<sup>38</sup> and 0.5% reproducibility on any given peak was achieved.

**Quantum Yield Determinations.** Quantum yields were determined with the microbench apparatus previously described.<sup>39</sup> Light absorption was measured with use of the previously reported electronic actinometer,<sup>40</sup> and all runs were calibrated with ferrioxalate actinometry.<sup>41</sup> Analyses were performed by using HPLC analysis as described above. In each case runs were made to varying conversions and the efficiencies extrapolated to 0% conversion. Sensitizer concentrations were adjusted high enough to effect efficient energy transfer but low enough to preclude singlet transfer. Table V summarizes individual runs.

**Quenching Runs.** These were run as in the direct photolyses, with

cyclohexadiene present as the triplet quencher. These runs are summarized in Table VI.

**Acknowledgment.** Support of this research by NIH Grant GM07487, the National Science Foundation, and a fellowship to X.J.H. from the People's Republic of China is gratefully acknowledged. The synthetic aspects of this research were supported by NIH while the mechanistic portions were supported by NSF.

**Registry No.** 1, 98509-43-4; 2, 98509-47-8; 6a, 98509-44-5; 6b, 98575-32-7; 7, 98509-45-6; 8, 41248-23-1; 9, 98509-39-8; 10, 98509-40-1; 10 tosylhydrazone, 98509-41-2; 11, 98509-42-3; 12, 98509-46-7; 13, 34780-08-0; 14, 98509-48-9; 15, 98509-49-0; CH<sub>3</sub>C(O)CH=CH<sub>2</sub>, 78-94-4; (Bu<sub>3</sub>P)<sub>4</sub>Cu<sup>+</sup>I<sup>-</sup>, 62566-04-5; *p*-PhC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 2567-29-5; 4-bromobiphenyl, 92-66-0; *p*-toluenesulfonylhydrazide, 1576-35-8; 1,2-bis(biphenyl-4-yl)-2-ethanone, 1694-24-2.

## Photochemical Rearrangements of Naphthyl-Substituted Enones—Mechanistic and Exploratory Organic Photochemistry<sup>1,2</sup>

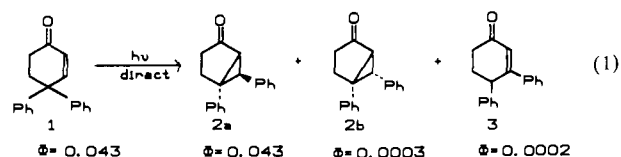
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Contribution from the Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706. Received November 6, 1984

**Abstract:** The photochemistry of 4,4-di( $\alpha$ -naphthyl)cyclohexenone and 4,4-di( $\beta$ -naphthyl)cyclohexenone was investigated in order to ascertain the effect of having internally bonded moieties which, as external chromophores, would ordinarily serve as triplet quenchers. Not only did the 4-arylcyclohexenone rearrangement proceed normally despite the presence of low triplet energy naphthyl groups, but the reactions proved to be extraordinarily efficient. Thus irradiation of the di- $\alpha$ -naphthyl enone led to *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one and 3,4-di( $\alpha$ -naphthyl)cyclohex-2-enone in a 1:1.2 ratio and with quantum efficiencies of 0.46 and 0.54, respectively. Direct irradiation of the di- $\beta$ -naphthyl enone afforded *trans*- and *cis*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one in a 19:1 ratio and with quantum yields of 0.38 and 0.02, respectively. Both the  $\alpha$  and  $\beta$  reactants were sensitized with xanthone ( $E_T = 74$  kcal/mol) and thioxanthone ( $E_T = 65.5$  kcal/mol). Independent of the sensitizer employed, each isomer afforded the same products observed in the direct irradiations and with the same quantum efficiencies. Thus, as in previously studied examples, the 4-aryl enone rearrangement leads preferentially to the *trans* stereoisomers of the bicyclic products. The efficiencies of the naphthyl isomers, however, are higher, totalling unity in the case of the  $\alpha$ -isomer. Identity of the direct irradiation and sensitized reaction results strongly indicated triplets as the reacting species. Triplet involvement was confirmed by cyclohexadiene and *di-tert*-butylnitroxyl quenching. Stern-Volmer treatment led to triplet rearrangement rates of  $1.7 \times 10^8$  and  $5.5 \times 10^7$  s<sup>-1</sup> for the  $\alpha$ - and  $\beta$ -naphthyl enones, respectively, and to rather similar total rate of triplet dissipation,  $1.7 \times 10^8$  and  $1.4 \times 10^8$  s<sup>-1</sup>, respectively. These decay rates are somewhat lower than that for the previously studied diphenylcyclohexenone ( $5.8 \times 10^8$  s<sup>-1</sup>), but the rates of rearrangement are greater than that ( $2.3 \times 10^7$  s<sup>-1</sup>) for the diphenyl enone with the  $\alpha$ -isomer being the most rapid. The ability to migrate thus is in the following order:  $\alpha$ -naphthyl >  $\beta$ -naphthyl > phenyl. The reaction mechanism and reaction subtleties are discussed.

One rearrangement we reported quite some years ago was that of cyclohexenones substituted at carbon-4 with aryl groups.<sup>3</sup> Where the substituent was phenyl, a rearrangement resulted, leading mainly to 5,6-diphenylbicyclo[3.1.0]hexan-2-one as depicted in eq 1.<sup>3</sup> In addition, our studies have focussed attention on migratory aptitudes,<sup>4,5</sup> on excited state activation energies,<sup>6</sup>

and on dependence of efficiency and excited state rate on structure.<sup>7</sup> Most recently, however, we turned our attention to the



rearrangements of enones and dienones having C-4 groups with varying triplet excitation energies. In this connection we note that bichromophoric molecules have been of particular interest recently.<sup>8</sup> In our previous publication<sup>2b</sup> biphenyl was used. In

(1) This is Paper 145 of our photochemical series and 203 of our general papers.

(2) (a) For paper 143 of the series, note: Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539-2551. (b) For Paper 144, see: Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724-7732.

(3) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036-4042. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749-3760.

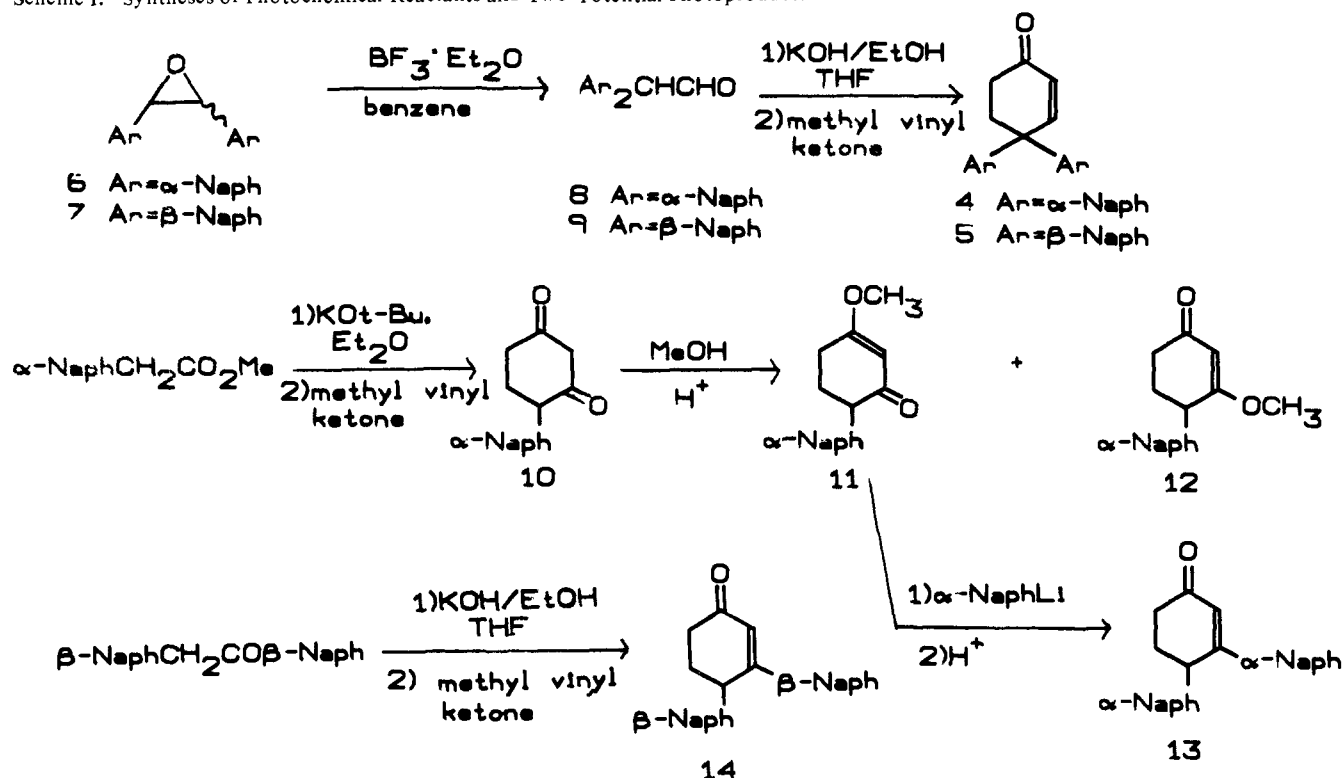
(4) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033-2047.

(5) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879-886.

(6) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887-896.

(7) (a) Zimmerman, H. E.; Sam, D. *J. Am. Chem. Soc.* **1966**, *88*, 4114-4116. (b) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954-966. (c) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 159-161. (d) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965-1973.

Scheme 1. Syntheses of Photochemical Reactants and Two Potential Photoproducts



the present study  $\alpha$ - and  $\beta$ -naphthyl groups were employed. The triplet excitation energy of naphthyl is lower than that of biphenyl (vide infra) and, additionally, naphthyl groups seemed likely to migrate with special ease. Hence, the behavior of the naphthyl systems promised to be of particular interest.

## Results

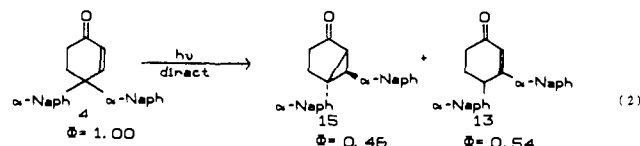
### Synthesis of Reactants of Interest.

The synthesis of the requisite 4,4-di- $\alpha$ - and 4,4-di- $\beta$ -naphthyl)cyclohexenones (**4** and **5**, respectively) began with the 1,2-disubstituted oxiranes **6** and **7**. These syntheses are outlined in Scheme I. Also included in Scheme I are descriptions of the preparations of two potential photoproducts **13** and **14**. In the synthesis of 3,4-di( $\alpha$ -naphthyl)cyclohexenone (**13**) two isomeric enol ethers (i.e., **11** and **12**) were obtained in approximately equal quantities independent of reaction conditions. However, the undesired isomer **12** was readily recycled to dione **10** which then was reused.

**Exploratory Photochemistry.** Direct irradiation of 4,4-di( $\alpha$ -naphthyl)cyclohexenone (**4**) led to two photoproducts. The first, mp 151–152.5 °C, had infrared and NMR spectra reminiscent of that of the *trans*-diphenyl bicyclic ketone **2a** encountered as the major product of irradiation of 4,4-diphenylcyclohex-2-enone (**1**), and a tentative assignment as *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one (**15**) seemed reasonable. The second photoproduct, mp 149–151.5 °C, was thought on similar spectral bases to be 3,4-di( $\alpha$ -naphthyl)cyclohex-2-enone (**13**). Indeed, this material proved identical with the authentic  $\alpha$ -naphthyl enone previously synthesized as noted above (note also Scheme I).

The skeletal assignment of the *trans*-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one structure **15** to the 151–152.5 °C photoproduct was confirmed by lithium–liquid ammonia reduction<sup>9</sup> of this compound to afford 2-( $\alpha$ -naphthylmethyl)-3- $\alpha$ -naphthylcyclopentanone **16** (note eq 3 in Scheme II) which was independently synthesized as depicted in eq 8 of Scheme II. The stereochemical assignments are justified below.

Hence the photochemistry of 4,4-di( $\alpha$ -naphthyl)cyclohexenone is as outlined in eq 2.



Our attention was next directed to the exploratory irradiation of 4,4-di( $\beta$ -naphthyl)cyclohexenone (**5**). Again, two photoproducts resulted, these with melting points of 144.5–146 and 187–188.5 °C. Application, again, of lithium–liquid ammonia degradation to the 146 °C photoproduct led to 3-( $\beta$ -naphthylmethyl)-3- $\beta$ -naphthylcyclopentanone (**18**) and also *cis*-3,4-di( $\beta$ -naphthyl)cyclohexanone **19**; note eq 4 in Scheme II. The two degradation products were synthesized as depicted in eq 6 and 7 of this scheme. The lithium–liquid ammonia degradation, along with the NMR data (vide infra), elucidated the carbon skeleton of the 144.5–146 °C photoproduct and led to its being recognized as *trans*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one (**17**).

The 188.5 °C photoproduct was subjected to the same lithium–liquid ammonia conditions (note eq 5 in Scheme II) and afforded the previously synthesized (vide supra) 3-( $\beta$ -naphthylmethyl)-3- $\beta$ -naphthylcyclopentanone (**18**); note eq 7. This degradation, along with the NMR data, established the structure of the 187 °C photoproduct as *cis*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one (**20**). Again, the stereochemical assignment is considered in a separate section below.

Hence the exploratory photochemistry of 4,4-di( $\beta$ -naphthyl)cyclohexenone is as described in eq 9.

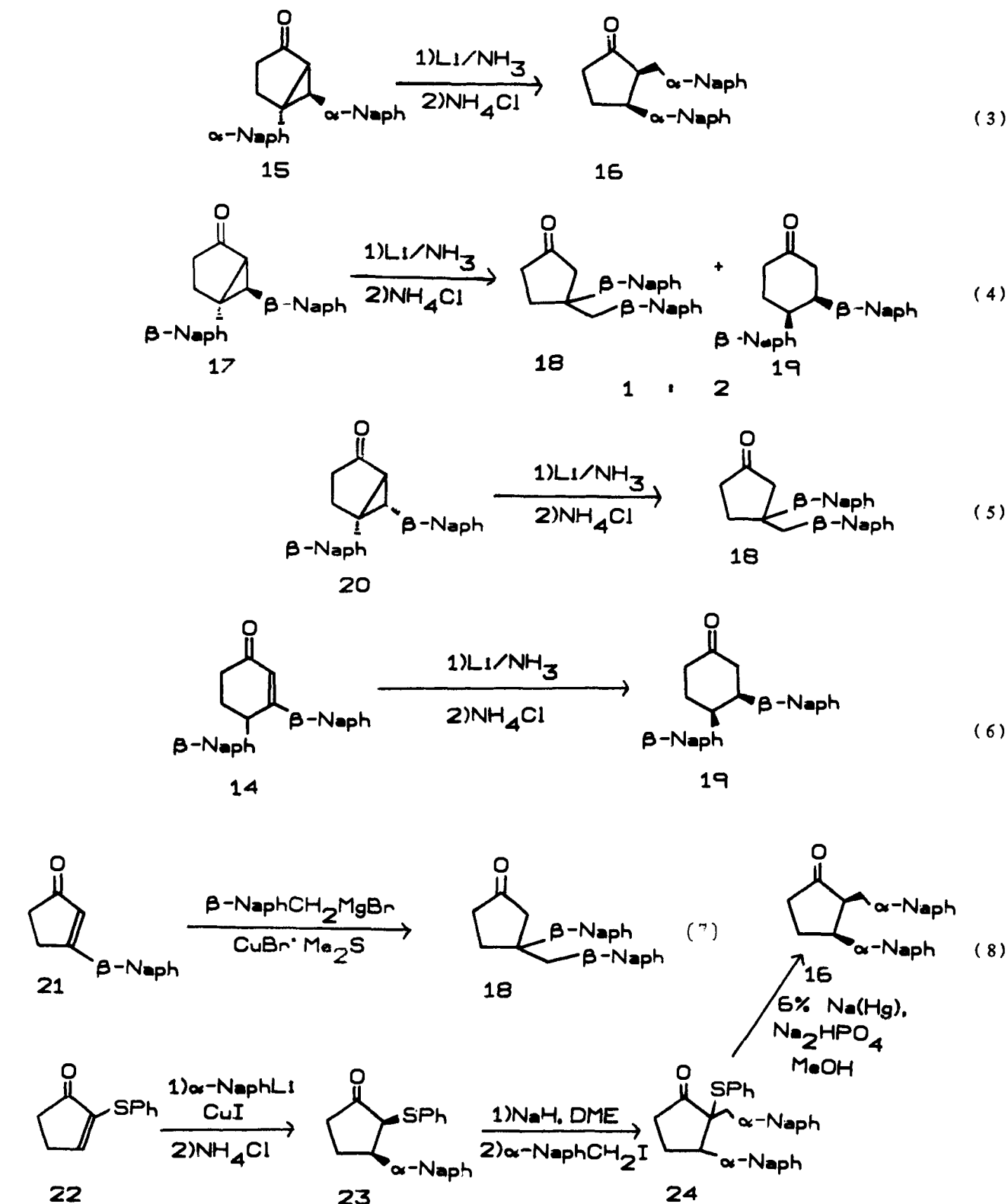
**Photochemical Reaction Stereochemistry.** A further item requiring consideration is the reaction stereochemistry. The structure elucidations described for the bicyclic photoproducts **15**, **17**, and **20** in Scheme II do not differentiate between *cis*- and *trans*-dinaphthyl configurations. Table I summarizes the 1,6-H,H coupling for a series of disubstituted bicyclo[3.1.0]hexanones. Thus all of the *trans* coupling constants (i.e., as in the *cis* bicyclic

(8) Note ref 2b for leading references to bichromophoric systems.

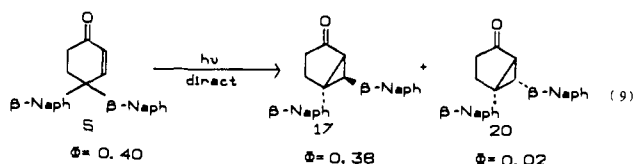
(9) Zimmerman, H. E.; Hancock, K. G.; Licke, G. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911.

(10) (a) Graham, J. D.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 2249–2252. (b) Note also: Meilboom, S.; Snyder, L. C. *J. Am. Chem. Soc.* **1967**, *89*, 1038–1039.

Scheme II. Structure Elucidation of the Bicyclic Photoproducts



ketones) are circa 4 Hz while the *cis* coupling constants in the *trans* bicyclic ketones are ca. 10 Hz. This is in agreement with the observation of Graham and Rogers,<sup>10a</sup> who reported a series



of *cis*- and *trans*-cyclopropane coupling constants to average 5.7 Hz for *trans* and 8.4 Hz for *cis*. Hence a clear differentiation of *cis* and *trans* stereoisomers is based on the consistent pattern in this table.

In our past cyclohexenone studies, it was observed that the *trans*-5,6-diarylbicyclo[3.1.0]hexanone was invariably kinetically preferred over the *cis* stereoisomer. This, again, is seen to be the case as shown in eq 2 and 9.

**Multiplicity and Quantum Yield.** In our previous studies<sup>2b,3b,4-6</sup> a variety of 4-arylcyclohexenones were shown to utilize the  $n-\pi^*$

Table I. Cyclopropane Coupling Constants

compound	$J_{1,6}(\text{cis})$ , Hz	$J_{1,6}(\text{trans})$ , Hz	ref
5,6-diphenyl bicyclic ketones, <b>2a</b> , <b>2b</b>	4.50	9.55	2b
5,6-dianisyl bicyclic ketones, <b>25a</b> , <b>25b</b>	4.0	10.0	4
5,6-dicyanophenyl bicyclic ketones, <b>26a</b> , <b>26b</b>	3.0	10.0	4
5,6-dibiphenyl bicyclic ketone, <b>27a</b> , <b>27b</b>	4.30	10.10	2b
5,6-di- $\alpha$ -naphthyl bicyclic ketones, <b>15</b>	<i>b</i>	9.56	<i>a</i>
5,6-di- $\beta$ -naphthyl bicyclic ketones, <b>17</b> , <b>20</b>	4.00	10.00	<i>a</i>

<sup>a</sup>This publication. <sup>b</sup>Cis isomer not available.

Table II. Triplet Energies as Measured by Phosphorescence

compound	$E_T$ , kcal/mol
4,4-di-( $\alpha$ -naphthyl)cyclohexenone ( <b>4</b> )	60.8
4,4-di-( $\beta$ -naphthyl)cyclohexenone ( <b>5</b> )	61.6

triplet as the reactive species which rearranged. In the present instance it appeared necessary again to determine the reaction multiplicity.

Sensitization was carried out on both the  $\alpha$  and the  $\beta$  enone (i.e. **4** and **5**) rearrangements with xanthone ( $E_T = 74$  kcal/mol<sup>11</sup>) under conditions where >98% of the incident light was absorbed by the sensitizer. This led to isolation of the same photoproducts observed on direct irradiation (i.e., without sensitizer). This provides necessary but not sufficient evidence that on direct irradiation it is the triplet which is the reactive species.

In this connection, the phosphorescence and fluorescence emission spectra were of considerable interest in understanding the electronics of the enones. At 77 K in MCIP glass (note Experimental Section) typical naphthalene-like phosphorescence emission was observed for both the  $\alpha$ - and the  $\beta$ -naphthyl enones **4** and **5**; note Table II. Remarkably, the triplet energy of these enones was within 1 kcal of the 60-kcal/mol value for naphthalene itself. This suggests that it is valid to treat the naphthyl and enone chromophores as separate (vide infra). The fluorescence emission for both enones was typically naphthalene-like. For the  $\alpha$  and  $\beta$  isomers the intensity was 1/10000 and 1/1020 that of naphthalene (see Experimental Section).

More information regarding triplet intervention came from low conversion sensitized runs where kinetic product distributions resulted. The primary purpose of these runs was the determination of reaction quantum yields. However, relevant to the present discussion, we note that in these runs product distributions were encountered which were identical with those observed in the direct irradiation counterparts. The identity of two such "fingerprints" has been proposed<sup>3b,4,7b,9</sup> to signify the identity of the reacting species involved in two experiments. Hence we can conclude that the triplet is the species reacting in the direct irradiations of the  $\alpha$ - and  $\beta$ -naphthyl enones **4** and **5**.

The direct and sensitized quantum yields are summarized in Table III. In each case runs were made to ever decreasing conversions in the range of 8 to 0.75% and then extrapolated to zero conversion. Primarily in the case of the direct  $\alpha$ -naphthyl enone irradiations, the determined quantum yields were sensitive to the extent of conversion due to product reactivity. In the remaining runs, the quantum yields were relatively insensitive to extent of conversion. However, such data are essential to ascertaining that quantum yields are not lowered by product light absorption.

One item needs present commentary. Thus, thioxanthone sensitization was carried out with the idea that its triplet energy of 65.5 kcal/mol<sup>12a</sup> is intermediate between the 68.5 kcal/mol enone<sup>3b</sup> triplet energy and the 60 kcal/mol naphthyl triplet energy.<sup>12b,c</sup> We note the interesting result in Table III that the triplet efficiencies with thioxanthone are within experimental error of

Table III. Tabulation of Direct and Sensitized Quantum Yields

enone reactant	sensitizer	product	quantum yield <sup>a</sup>
$\alpha$ -naphthyl <b>4</b>	none	$\alpha$ -trans-bicyclic <b>15</b>	0.46 (0.43)
		$\alpha$ -3,4-enone <b>13</b>	0.54 (0.57)
$\alpha$ -naphthyl <b>4</b>	xanthone	$\alpha$ -trans-bicyclic <b>15</b>	0.43 (0.45)
		$\alpha$ -3,4-enone <b>13</b>	0.56 (0.53)
$\alpha$ -naphthyl <b>4</b>	thioxanthone	$\alpha$ -trans-bicyclic <b>15</b>	0.40 (0.42)
		$\alpha$ -3,4-enone <b>13</b>	0.60 (0.58)
$\beta$ -naphthyl <b>5</b>	none	$\beta$ -trans-bicyclic <b>17</b>	0.38 (0.40)
		$\beta$ -cis-bicyclic <b>20</b>	0.02 (0.02)
$\beta$ -naphthyl <b>5</b>	xanthone	$\beta$ -trans-bicyclic <b>17</b>	0.39 (0.41)
		$\beta$ -cis-bicyclic <b>20</b>	0.02 (0.02)
$\beta$ -naphthyl <b>5</b>	thioxanthone	$\beta$ -trans-bicyclic <b>17</b>	0.36 (0.39)
		$\beta$ -cis-bicyclic <b>20</b>	0.02 (0.02)

<sup>a</sup>The unparenthesized quantum yields are for runs in benzene while those in parentheses are runs in *tert*-butyl alcohol.

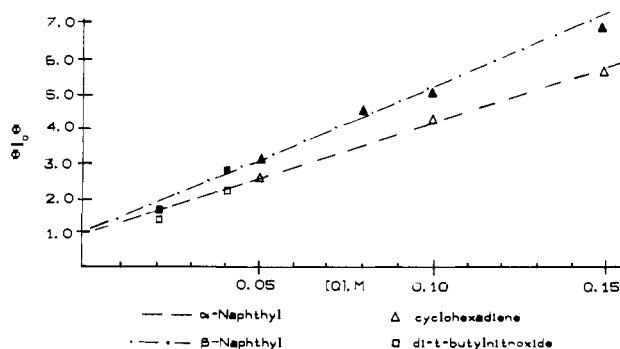


Figure 1. Stern-Volmer quenching behavior of the naphthyl cyclohexenones.

those obtained with the 74 kcal/mol xanthone triplet,<sup>11</sup> which is capable of efficiently exciting either chromophore and also within experimental error of the direct irradiations where the competition for light leads to preferential light absorption by the naphthyl moiety.

**Determination of Excited-State Rates.** As has been noted in a number of our previous publications<sup>13</sup> excited-state reactivity is most reliably correlated with excited-state rate constants rather than with quantum yields. To obtain the desired rate constants, the Stern-Volmer quenching experiments used cyclohexadiene ( $E_T = 52.4$  kcal/mol<sup>14</sup>) and also di(*tert*-butyl)nitroxyl<sup>15</sup> as quenchers; note Figure 1. The usual treatment<sup>16</sup> affords the slope as  $k_q\tau$ . This, together with the assumption that quenching is diffusion controlled with a bimolecular rate of  $6 \times 10^9$  s<sup>-1</sup>,<sup>17</sup> affords values of  ${}^3\tau$  and  ${}^3k_{d(\text{tot})} = 1/\tau$  for the  $\alpha$  and  $\beta$  enone triplet rearrangements as summarized in Table IV.

Additionally, with the assumption of unit efficiency of inter-system crossing, one can obtain the rate of triplet rearrangement

(13) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 439-449. (b) Also see ref 7d and 12c. Zimmerman, H. E.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 3646-3653.

(14) (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.

(15) Hoffmann, A. K.; Feldman, A. M.; Gelblum, E.; Hodgson, W. J. *J. Am. Chem. Soc.* **1964**, *86*, 639-646.

(16) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183-186.

(11) Pownall, H. S.; Huber, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 6429-6436.

(12) (a) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537-4540. (b) Marichetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768-777. (c) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1043-1052.

**Table IV.** Triplet Lifetimes, Decay, and Reaction Rate Constants<sup>a</sup>

enone	$\tau$ , ns	$^3k_{d(\text{tot})}$ , s <sup>-1</sup>	$^3k_r$ , s <sup>-1</sup>
$\alpha$ -naphthyl enone <b>4</b>	6.0	$1.66 \times 10^8$	$1.68 \times 10^8$
$\beta$ -naphthyl enone <b>5</b>	7.3	$1.36 \times 10^8$	$5.46 \times 10^7$

<sup>a</sup>Solvent benzene.**Table V.** MMPI Comparison of Cis and Trans Bicyclics

compound	steric energy, kcal/mol
<i>cis</i> - $\alpha$ -dinaphthyl bicyclic <b>28</b>	42.8
<i>trans</i> - $\alpha$ -dinaphthyl bicyclic <b>15</b>	41.5
<i>cis</i> - $\beta$ -dinaphthyl bicyclic <b>20</b>	41.0
<i>trans</i> - $\beta$ -dinaphthyl bicyclic <b>17</b>	38.7
<i>cis</i> -diphenyl bicyclic <b>2b</b>	27.4
<i>trans</i> -diphenyl bicyclic <b>2a</b>	24.9

as  $k_r = ({}^3\phi_r)({}^3k_{d(\text{tot})})$ . These rates are also included in Table IV.

That perfectly efficient intersystem crossing is a valid assumption is immediately apparent in the case of the  $\alpha$ -naphthyl enone **4**, since the reaction quantum yield is unity. In the case of the  $\beta$  enone **5**, the same conclusion is justified by the observation that with xanthone sensitization, where the triplet is generated exothermically, the same quantum yield results as in the direct irradiation runs (note Table III).

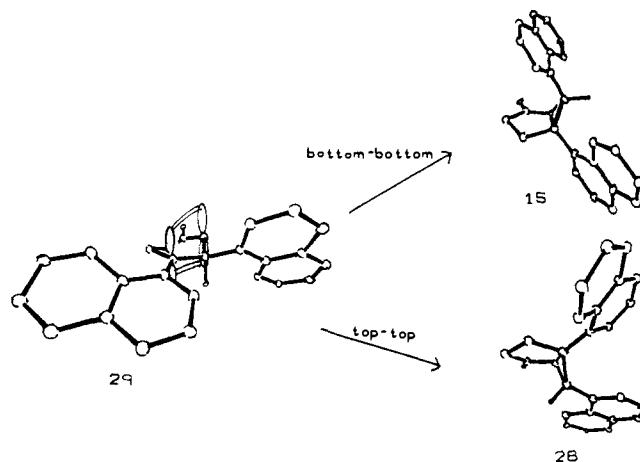
### Interpretative Discussion

**The Reaction Course.** The first observation requiring commentary deals with the photochemistry of the 4,4-di( $\alpha$ -naphthyl)cyclohexenone **4**. Here we note the absence of the *cis* isomer of 5,6-di( $\alpha$ -naphthyl)bicyclic ketone **15** and the relatively large proportion of 3,4-dinaphthyl enone **13**. Throughout, photolysis of 4,4-diarylcyclohexenones<sup>2b,3,4,7b</sup> has led preferentially to the *trans* bicyclo[3.1.0] isomer. In the case of the 4,4-diphenylcyclohexenone **1** the ratio of *trans* to *cis* bicyclic products was 143:1 and 3,4-diphenylcyclohexenone **3** was a minor product as well (note eq 1).

The absence of *cis* isomer is not due to a large difference in steric repulsions between isomers. This was most readily evidenced by use of MMPI molecular mechanics.<sup>18</sup> Note Table V which indicates that the steric differences between *cis* and *trans* isomers are relatively small. The *trans* isomers, having separated aryl groups but the aryl group endo to the five ring, have lower steric energies.

The preferential formation of the *trans* isomers seems most likely due to an electronic requirement for inversion of configuration at C-4 in the reacting enone as suggested in our earlier efforts.<sup>3b</sup> Furthermore, to the extent that the reaction in the present example is better described as a di- $\pi$ -methane rearrangement (vide infra), it is germane that the "methane carbon" in di- $\pi$ -methane systems is known<sup>19</sup> to be inverted in that rearrangement as well.

However, the complete absence of *cis* isomer in the  $\alpha$ -naphthyl rearrangements contrasts with the  $\beta$ -naphthyl example and with all the previously studied cases.<sup>2b,3,4,7b</sup> Table V shows that the *cis*- $\alpha$ -dinaphthyl bicyclic ketone is not much more severely hin-

**Figure 2.** Three-dimensional picture of product formation.

dered than the other *cis* bicyclic products. Hence product strain must not be a factor.

An intriguing point comes from inspection of Figure 2 which depicts closure of the "open diradical" species **29** resulting from aryl migration in the excited enone. This may be the route leading the enones to the *cis* bicyclic and 3,4-diarylenone byproducts. The specific example of  $\alpha$ -naphthyl is shown. The diradical may form a three-ring by overlap of the bottom C-2 and C-4 p-orbital lobes to engender the *trans* bicyclic product **15** or by overlap of the top p-orbital lobes to form *cis* bicyclic product **28**. However, as biradical **29** forms bicyclic product, the  $\alpha$ -naphthyl group at C-4 needs to continue to overlap with the developing  $\sigma$  bond of the three-ring. This leads to a much more severe naphthyl-naphthyl steric interaction as *cis* bicyclic product is being formed than either in the original diradical or in the fully formed *cis* bicyclic product **28**. Thus the effect of aryl-aryl interaction is magnified and  $\alpha$ -naphthyl becomes the most stereoselective.

**Reaction Multiplicity and Efficiency.** The reaction multiplicity being triplet is in complete accord with all of the previously studied aryl enone rearrangements.<sup>2b,3,4,7b</sup> Most remarkable, however, are the very high reaction efficiencies of the rearrangement of the naphthyl enones **4** and **5** with quantum yields of 1.00 for the  $\alpha$ -naphthyl reactant and 0.40 for the  $\beta$  isomer. Table VI compares quantum yields for the various known enone rearrangements. We note a gradual increase in reaction efficiencies as the conjugating ability of the aromatic group at C-4 of the enones is increased. Phenyl substitution affords the least efficient enone, and  $\alpha$ -naphthyl substitution gives the most efficient enone.

**Significance of Quantum Yield and Rate Measurements.** In most photochemical studies a single chromophore is involved. Thus in our previous studies of 4,4-diphenylcyclohexenone, the enone moiety selectively absorbed the incident light, was converted by intersystem crossing to triplet multiplicity, and then induced migration of a phenyl group. Hence, not only the singlet but also the triplet excitation energy of the enone chromophore is much lower than that of the phenyl groups, and electronic excitation is anticipated to be concentrated in the enone moiety.

More generally, as in the present study, more than one chromophore may possibly be excited. Thus, the naphthyl groups in the naphthyl enones **4** and **5** capture essentially all of the incident light at the irradiation wavelengths. Nevertheless, the enone moiety should be of lower singlet energy (ca. 76 kcal/mol<sup>20a</sup>) compared with naphthyl (ca. 90 kcal/mol<sup>20b</sup>), and singlet energy transfer to the enone moiety should be rapid and followed by very facile intersystem crossing at the enone end of the molecule. That such energy transfer is rapid has precedent in our study<sup>21</sup> of singlet

(17) (a) A value of  $5.0 \times 10^9$  M s<sup>-1</sup> for the rate of diffusion in benzene has been measured. (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769-4777. (c) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 1245-1251. (d) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232-2238. (e) Wagner, P. J.; Spoerke, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4437-4440. (f) Scaiano et al. (Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539-1542) have reported a value of  $6.0 \times 10^9$  L M<sup>-1</sup> s<sup>-1</sup> for the quenching of *p*-methoxyacetophenone by oxygen in benzene and similar values for analogous quenching of various ketones by dienes in this solvent.

(18) (a) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893-3898. (b) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100-5106. (c) MMPI was run on a VAX/750 with a slightly modified "Tribble" system.<sup>18d</sup> (d) Pensaks, D. *Ind. Res. Dev.* **1983**, *25*, 74-78.

(19) (a) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 1974-1976. (b) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630-4643. (c) Zimmerman, H. E.; Gannett, T. P.; Keck, G. E. *J. Am. Chem. Soc.* **1978**, *100*, 323-324. (d) Zimmerman, H. E.; Gannett, T. P.; Keck, G. E. *J. Org. Chem.* **1979**, *44*, 1982-1989.

(20) (a) The singlet energy of cyclohex-2-en-1-one was found to be 80 kcal/mol: Torri, J.; Azzaro, M. *Tetrahedron Lett.* **1975**, 3251-3253. (b) The singlet energy of naphthalene was found to be 90 kcal/mol: Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley, New York, 1970; p 70.

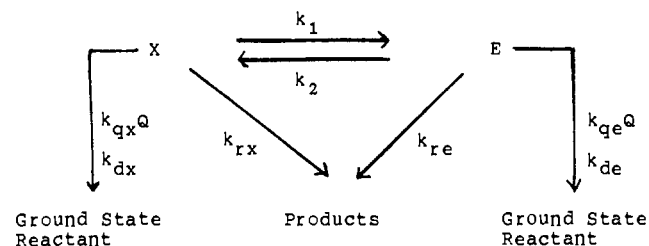
(21) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933-3951.

Table VI. Summary of Quantum Yields for 4,4-Diarylcyclohexenones

compound	$\phi_{\text{dis}}$	$k_r$	$k_{\text{dtot}}$	ref
4,4-diphenylcyclohexenone <b>1</b>	0.043	$2.3 \times 10^7$	$5.3 \times 10^8$	3b <sup>b</sup>
4-( <i>p</i> -cyanophenyl)-4-phenylcyclohexenone <b>30</b>	0.19	$2.2 \times 10^8$	$1.1 \times 10^9$	5 <sup>b</sup>
4,4-dibiphenylcyclohexenone <b>28</b>	0.36	$1.3 \times 10^8$	$3.4 \times 10^8$	2b
4,4-di-( $\beta$ -naphthyl)cyclohexenone <b>5</b>	0.40	$5.5 \times 10^7$	$1.4 \times 10^8$	<i>a</i>
4,4-di-( $\alpha$ -naphthyl)cyclohexenone <b>4</b>	1.00	$1.7 \times 10^8$	$1.7 \times 10^8$	<i>a</i>

<sup>a</sup> This work. <sup>b</sup> These values have been calculated with use of the current quenching rate used.

## Scheme III. General Kinetic Outline



transfer in rodlike molecules from naphthyl to acetyl and benzoyl groups ca. 7 Å distant; these rates were above  $10^9 \text{ s}^{-1}$ . More directly, the fluorescence intensity observed for the  $\alpha$  and  $\beta$  enones was very weak (1/1000th; note Experimental Section) in contrast to simple naphthalenes thus paralleling the behavior in the case of the rodlike molecules. We note that the rate of intersystem crossing for naphthalene<sup>22a</sup> is  $5 \times 10^6 \text{ s}^{-1}$  while that for conjugated ketones is of the order of  $10^{11}$ – $10^{12} \text{ s}^{-1}$ .<sup>22b</sup> Thus it seems likely that at time zero, when intersystem crossing to afford a triplet first occurs, it is the enone triplet chromophore which is engendered.

As in the accompanying paper,<sup>2b</sup> we need to comment on the assignment of 69 kcal/mol to the enone triplet involved in the rearrangement. Thus evidence for a twisted cyclohexenone triplet of energy 61–63 kcal/mol has been presented on the basis of a laser-detected transient.<sup>23,24</sup> However, Pienta<sup>23</sup> and also Schuster, Bonneau, and Jousot-Dubien<sup>23</sup> found that this triplet is not quenched by cyclohexadiene and is most likely not responsible for the type A cyclohexenone rearrangements.<sup>7c,d</sup> With the evidence presently in hand, there is no reason yet to assume that this triplet is responsible for the presently studied rearrangement, which also is quenched by cyclohexadiene. A final conclusion must await further information about the identity of the transient.

A further point is that the enone rearrangements with naphthalene (i.e.,  $E_T = 61 \text{ kcal/mol}$ ) chromophores studied here are perfectly efficiently sensitized by thioxanthone (66 kcal/mol<sup>11</sup>). In contrast, in our previous study,<sup>2b</sup> the analogous systems incorporating biphenyl groups ( $E_T = 69 \text{ kcal/mol}$ ) exhibited markedly diminished quantum efficiencies with thioxanthone. Since both systems incorporate the enone chromophore, we must attribute the difference to the presence of the naphthyl moiety in the currently studied system in place of the higher energy biphenyl group.<sup>25</sup> Now, if a lower energy (i.e., 61–63 kcal/mol) enone moiety were available and could accept energy and lead to reaction, it should do so competitively with biphenyl, and the inefficient sensitization observed in the biphenyl case<sup>2b</sup> should not be observed. Hence, the simplest rationale is that a twisted cyclohexenone moiety does not lead to reaction.

(22) (a) For naphthalene, a value of  $5 \times 10^6 \text{ s}^{-1}$  has been reported: Kasha, M. *Discuss. Faraday Soc.* **1950**, 9, 14–19. (b) For benzophenone, a value of  $10^{11}$  has been reported: Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, 61, 2500–2511. (c) For acetophenone, a value of  $10^{12}$  has been reported: Hirata, Y.; Lim, E. C. *Chem. Phys. Lett.* **1980**, 167–170. See also: Stockburger, M. Z. *Phys. Chem. NF* **1962**, 31, 350–365.

(23) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Jousot-Dubien, J. *J. Am. Chem. Soc.* **1984**, 106, 2706–2707.

(24) Pienta, N. J. *J. Am. Chem. Soc.* **1984**, 106, 2704–2705.

(25) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, 89, 2820–2825.

(26) (a) Analogous kinetics have been reported by P. Wagner, for the case of initial excitation to afford one state followed by possible interconversion and reaction of both. (b) Wagner, P. J. "Creation and Detection of the Excited State"; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Chapter 4, pp 173–212. (c) Shetlar, M. *Mol. Photochem.* **1973**, 5, 311.

In the preceding publication<sup>2b</sup> the kinetics of a reacting bi-chromophoric system was discussed. It was noted that, in general, the kinetics of an enone reaction may be depicted as in Scheme III.

Here E is the molecule with a triplet excited enone moiety and X is the molecule with a triplet excited aryl group. Also,  $L_x$  and  $L_e$  are the fractions of the (e.g., triplet) excitation at time zero introduced in the X and E moieties, respectively.  $I_x$  and  $I_e$  are the total number of milliEinstein of light effectively transferred to excitation in the two moieties while  $I$  is the total amount of light absorbed.

Also, we define

$$K_e = k_{re} + k_{de} \quad (10a)$$

$$K_x = k_{rx} + k_{dx} \quad (10b)$$

$$L_x = I_x/I \text{ and } L_e = I_e/I, \text{ while } L_e + L_x = 1 \quad (10c)$$

Then the total quantum yield in the presence of quencher is given by<sup>26</sup>

$$\phi = \phi_{\text{isc}} \left[ \frac{[(K_e + k_{qe}Q)L_x + k_2]k_{rx} + [(K_x + k_{qx}Q)L_e + k_1]k_{re}}{(K_x + k_1 + k_{qx}Q)(K_e + k_2 + k_{qe}Q) - k_1k_2} \right] \quad (11)$$

The unquenched efficiency is

$$\phi_0 = \phi_{\text{isc}} \left[ \frac{[K_e L_x + k_2]k_{rx} + [K_x L_e + k_1]k_{re}}{(K_x + k_1)(K_e + k_2) - k_1k_2} \right] \quad (12)$$

Thus

$$\phi_0/\phi = AB \quad (13)$$

where

$$A = \left[ 1 + \frac{(k_{qe}k_{rx}L_x + k_{qx}k_{re}L_e)Q}{[K_e L_x + k_2]k_{rx} + [K_x L_e + k_1]k_{re}} \right]^{-1} \quad (14a)$$

$$B = \left[ 1 + \frac{[k_{qe}(K_x + k_1) + k_{qx}(K_e + k_2)]Q + k_{qe}k_{qx}Q^2}{k_1K_e + k_2K_x + K_eK_x} \right] \quad (14b)$$

However, there are four constraints in the enones presently under consideration: (1) The quantum yields are independent of  $L_e$  vs.  $L_x$ , as seen from the independence of product distribution and efficiencies on direct vs. sensitized reaction and also which sensitizer is used. (2) The Stern-Volmer plots are linear. (3) The quantum yield is unity for the  $\alpha$ -naphthyl case. (4) In view of the 61 kcal/mol naphthyl  $T_1$  energy and the 69 kcal/mol enone value, the ratio of  $k_1$  to  $k_2$  is circa  $10^{-6}$ .

In the molecules now under study, as noted above, localization of triplet excitation at intersystem crossing time zero is likely, but not certain, to be in the enone moiety in view of the rapid rate of intersystem crossing in enones as a consequence of spin-orbit coupling. Also, in sensitization experiments, especially with the low-energy (i.e., 65.5 kcal/mol) thioxanthone sensitizer, one would anticipate preferential transfer of triplet excitation to the naphthyl moiety.

Further, since  $k_2$  is very large compared with  $k_1$ , we can assume that the enone excited triplet (i.e.,  $T_2$ ) may convert to the naphthyl

excited species (i.e.,  $T_1$ ) but not conversely. Also, with a unit efficiency for the  $\alpha$  isomer the  $k_d$ 's cannot be competitive.

This information, coupled with the requirement of Stern-Volmer linearity, permits simplification of the kinetic eq 11-14. This simplification is tantamount to realization that conversion of  $T_2$  to  $T_1$  is much faster than any of the competitive processes.

That a rapid  $k_2$  is reasonable is seen by analogy. Thus,  $k_2$  corresponds to the rate of intramolecular triplet transfer between the naphthyl and enone moieties in enones **4** and **5**. Triplet transfer to styryl ( $E_T = 60$  kcal/mol<sup>27</sup>) from benzoyl ( $E_T = 74$  kcal/mol<sup>27</sup>) in a series of molecules, with different numbers of methylene groups interposed, has been found to range between  $10^{10}$  and  $7 \times 10^{10}$  s<sup>-1</sup>; <sup>28a</sup> the latter, with one methylene interposed, is geometrically closest to the case at hand. A similar system was reported to have a rate greater than  $1-2 \times 10^{10}$  s<sup>-1</sup>. <sup>28b</sup>

Hence the assumption that  $k_2 > K_c$  and  $k_{qe}$  and that  $k_1$  is small in comparison with the other rate constants leads us to eq 15 and 16.

$$\phi = k_{rx}/K_x \quad (15)$$

$$\text{slope} = (k_q\tau)^{\text{empir}} = k_{qx}/K_x \quad (16)$$

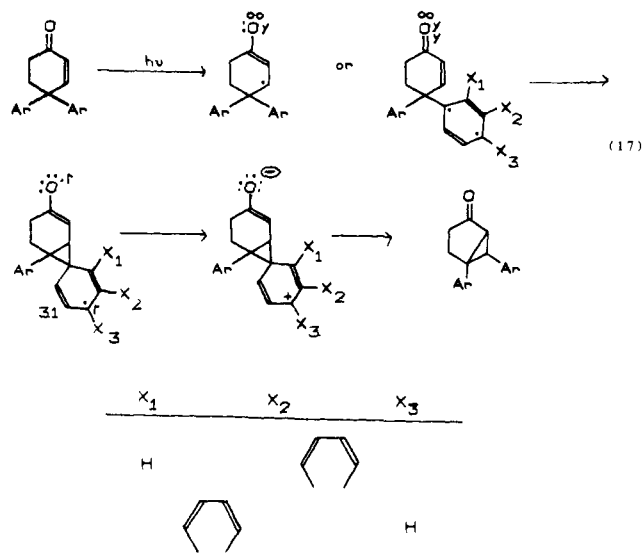
We see that these are just the usual expressions for the quantum yield and Stern-Volmer slope.<sup>26</sup>

With the naphthyl end of the molecule being excited as the rearrangement proceeds, we note that the reaction is really a di- $\pi$ -methane rearrangement<sup>29</sup> and thus the present example is at one end of the spectrum of 4-aryl enone rearrangements, the other end consisting of aryl migration being initiated by an  $n-\pi^*$  enone moiety.

Finally, there is an interesting point in the observation that the observed total rates of decay of 4,4-diarylcyclohexenones, with the aryl groups being phenyl,<sup>3b</sup> cyanophenyl,<sup>5</sup> biphenyl,<sup>2b</sup>  $\alpha$ - and  $\beta$ -naphthyl (this work)—all fall within a factor of 4. Yet the evidence is that there is a spectrum of behavior in which the phenyl example is a reaction of the  $n-\pi^*$  triplet with excitation in the enone end of the molecule and in which the naphthyl examples are more akin to di- $\pi$ -methane rearrangements with excitation initially in the aryl portion of the molecule. Further, the total decay of the  $\alpha$ -naphthyl enone **4** triplet is due to utilization of excited state by reaction while, in contrast, the total decay of the diphenyl enone **1** triplet is primarily attributable to reversion to ground-state reactant.

The common feature which leads to this relatively consistent rate of excited-state utilization, independent of whether the utilization is for reaction or return to ground state, seems to be the bridged diradical **31**. This diradical may intersystem cross to the corresponding (ground state) zwitterion which then either decays or proceeds on to product as shown in eq 17. Thus, while the energetics of reaching diradical **31** should differ somewhat, the rates of its decay to ground state should not differ too much. That a unique mode of decay is utilized is clear from the short 3.6-ns lifetime of the, e.g.,  $\alpha$ -naphthyl enone **5** compared with the 74- $\mu$ s lifetime of naphthalene itself.

There remains the question of the consequence of having reversion from such a diradical to reactant ground state. Thus, one might wonder about the significance of the measured  $k_r$ 's and  $\tau$ 's. However, many photochemical reactions proceed via diradicals and pericyclic equivalents where reversion to reactant ground state



is possible. Our approach has been to recognize that the  $k_r$ 's and  $\tau$ 's obtained are operational. In our preceding publication<sup>2b</sup> we noted that  $k_r$  and  $\tau$  are then described by eq 18 and 19. Here

$$\tau(\text{measured}) = \frac{(k_p + k_{-b} + k_{dd})}{(k_p + k_{-b} + k_{dd})(k_b + k_{dr}) - k_b k_{-b}} \quad (18)$$

$$k_r(\text{operational}) = (k_b k_p) / (k_p + k_{-b} + k_{dd}) \quad (19)$$

$k_b$  is the rate of excited-state bridging to afford the diradical,  $k_{-b}$  is the reverse of this step,  $k_p$  is the rate of diradical proceeding on to product,  $k_{dd}$  is the rate of decay of diradical back to reactant ground state, while  $k_{dr}$  is the rate of vertical excited-state decay. Thus the measured lifetime is an operational value which becomes  $(k_b + k_{dr})^{-1}$ , or the usual  $\tau$ , if  $k_{-b}$  vanishes. This has been assumed in our arylcyclohexenone mechanisms. The operational rate constants obtained give us the ordinary rate constant for bridging (i.e.,  $k_b$ ) multiplied by the probability of the diradical proceeding onward to product (i.e.,  $k_p / (k_p + k_{-b} + k_{dd})$ ).

**Theoretical Considerations.** The  $\alpha$  and  $\beta$  starting enones **4** and **5**, respectively, as well as the corresponding bridged biradicals **32** and **33** were subjected to MNDO<sup>30</sup> calculation with the aim of inspecting the difference between ground and excited bond orders following our  $\Delta P$  treatment.<sup>31</sup> The  $\Delta P$  matrix elements give a measure of distribution of excitation energy. At those molecular sites where there are large negative  $\Delta P$  elements, the bond orders are more antibonding in the excited state than in the ground state. The partition of excitation energy can be semi-quantitatively assessed by inspection of these elements. Figure 3 shows that in the reactant enones, electronic excitation is concentrated in the naphthyl moieties as might be anticipated. In contrast, in the bridged diradical species, the excitation energy becomes redistributed and concentrated in the three-ring and adjacent centers. This is similar to our findings for the di- $\pi$ -methane rearrangement where excitation becomes localized in the cyclopropyldicarbonyl diradical moiety as  $\pi-\pi$  bridging occurs.

In conclusion, it is seen that the 4-aryl enone rearrangement is a very general reaction with reactivity patterns which seem predictable. Thus reference to Table VI reveals that as stabilization of the bridged diradical is enhanced, the quantum efficiencies and the rates are increased. This accounts for the biphenyl enones being more reactive than 4,4-diphenylcyclohexenone (**1**) and for the  $\alpha$ -naphthyl enone **4** being more reactive than the  $\beta$ -naphthyl enone **5**.

(27) (a) A value of 61.7 kcal/mol has been reported: Bylina, A.; Grabowski, Z. R. *Trans. Faraday Soc.* **1969**, *65*, 458-461. (b) A 60 kcal/mol is given: Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *42*, 2129-2132. (c) A value of 73.6 kcal/mol has been reported for acetophenone while a value of 74.6 kcal/mol has been reported for propiophenone.<sup>10</sup>

(28) (a) Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153-1162. (b) Lamola, A. A.; Leermakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322-2329.

(29) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932-3933. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718-1727. (c) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (d) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531-551.

(30) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899-4912. (b) QCPE Program No. 455, Quantum Chemistry Program Exchange, Indiana University.

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Experimental Section<sup>32</sup>

**cis- and trans-1,2-Di( $\alpha$ -naphthyl)oxirane.**<sup>33</sup> To a solution of 15.5 g (55.4 mmol) of a mixture of *cis*- and *trans*-1,2-di( $\alpha$ -naphthyl)ethylene<sup>34</sup> dissolved in 100 mL of dry methylene chloride was added dropwise a solution of 15.3 g (80.3 mmol) of 40% peracetic acid and 0.94 g of sodium acetate trihydrate. The solution was stirred for 48 h, and basic workup<sup>32</sup> gave 13 g of a yellow oil which was recrystallized from methanol to give 11.4 g (65%) of a mixture of *cis*- and *trans*-1,2-di( $\alpha$ -naphthyl)oxirane. The mixture was adsorbed onto basic alumina and column chromatographed on a 2 m  $\times$  3 cm quartz column packed with basic alumina. The mixture was eluted with 10% ether/hexane to give 5.3 g of *cis*-1,2-di( $\alpha$ -naphthyl)oxirane which was recrystallized from cyclohexane to give 5.1 g (31%) of the *cis* oxirane, mp 140–141 °C, and 5.4 g of *trans*-1,2-di( $\alpha$ -naphthyl)oxirane which was recrystallized from cyclohexane to give 5.3 g (32%) of the *trans* oxirane, mp 168–169 °C. The spectral data for *cis*-1,2-di( $\alpha$ -naphthyl)oxirane were the following: IR (CHCl<sub>3</sub>) 3050, 1595, 1510, 1395, 1320, 1260, 1075, 1025, 900, 800 cm<sup>-1</sup>; H NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–8.12 (m, 14 H, arom), 4.48 (s, 2 H, CHOR); CMR (CDCl<sub>3</sub>)  $\delta$  60.452; MS, *m/e* 296.1201 (calcd for C<sub>22</sub>H<sub>16</sub>O, *m/e* 296.1200).

Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O: C, 89.14; H, 5.44. Found: C, 88.94; H, 5.50.

The spectral data for *trans*-1,2-di( $\alpha$ -naphthyl)oxirane were the following: IR (CHCl<sub>3</sub>) 3045, 3000, 1595, 1510, 1340, 1260, 1155, 1070, 1030, 900, 835, 785 cm<sup>-1</sup>; H NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, *J* = 8.0 Hz, 2 H, peri-H arom), 6.88–7.48 (m, 12 H, arom), 5.02 (s, 2 H, CHOR); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  58.956; MS, *m/e* 296.1201 (calcd for C<sub>22</sub>H<sub>16</sub>O, *m/e* 296.1200).

Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O: C, 89.14; H, 5.44. Found: C, 89.07; H, 5.54.

**2,2-Di( $\alpha$ -naphthyl)acetaldehyde.**<sup>35</sup> The product yield in this preparation was quite dependent on precise conditions. To a solution of 1.00 g (3.4 mmol) of a mixture of *cis*- and *trans*-1,2-di( $\alpha$ -naphthyl)oxirane in 10 mL of dry benzene was added 0.22 mL (1.8 mmol) of freshly distilled boron trifluoride etherate in a separatory funnel and the mixture was shaken twice. The solution was allowed to stand for 1.0 min when it was poured into 10 mL of water. Immediately, a white precipitate formed which was dissolved in methylene chloride. Neutral workup<sup>32</sup> gave 1.1 g of a cream-colored solid, mp 172–185 °C. The solid was recrystallized from chloroform to give 0.99 g (99%) of 2,2-di( $\alpha$ -naphthyl)acetaldehyde, mp 188–189 °C. The spectral data were the following: IR (CCl<sub>4</sub>) 3030, 2800, 2700, 1715 (C=O), 1590, 1500, 1390, 1370, 1020, 775 cm<sup>-1</sup>; H NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  10.05 (d, *J* = 1.5 Hz, 1 H, CHCHO), 7.15–7.71 (m, 14 H, arom), 6.24 (d, *J* = 1.5 Hz, 1 H, CHCHO); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  198.879 (C=O), 56.625; MS, *m/e* 296.1200 (calcd for C<sub>22</sub>H<sub>16</sub>O, *m/e* 296.1200).

Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O: C, 89.14; H, 5.44. Found: C, 88.98; H, 5.61.

**4,4-Di( $\alpha$ -naphthyl)cyclohex-2-en-1-one.** To a solution of 0.332 g (1.12 mmol) of 2,2-di( $\alpha$ -naphthyl)acetaldehyde dissolved in 5.5 mL of dry THF was added dropwise via syringe at -10 °C 0.115 mL (0.344 mmol) of 3.0 N KOH in absolute ethanol. The solution was allowed to stir an additional 10 min at this temperature when 0.124 mL (1.12 mmol) of methyl vinyl ketone was added dropwise with stirring. The solution was slowly warmed to room temperature, allowed to stir at room temperature for 24 h, and refluxed for 72 h. After the solution was cooled to room temperature, acidic–basic workup<sup>32</sup> gave 0.300 g of a red-brown oil which was purified via column chromatography. The solid was adsorbed on 5 mL of silica gel and placed on a 2.5 cm  $\times$  1 m quartz column eluting as

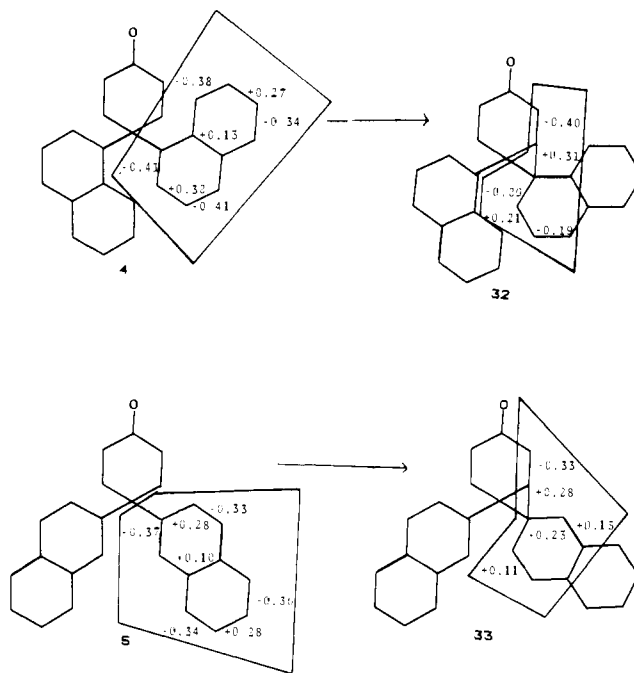


Figure 3.  $\Delta P$  delineation of excitation migration.

follows: 1, 500 mL, 50% hexane/methylene chloride, nil; 2, 300 mL, 50% hexane/methylene chloride, starting aldehyde; 3, 150 mL, methylene chloride, enone, 0.200 g. Recrystallization from ether afforded 0.189 g (49%) of 4,4-di( $\alpha$ -naphthyl)cyclohexenone as white needles, mp 190–190.5 °C. The spectral data were the following: IR (CCl<sub>4</sub>) 3040, 2950, 1690 (C=O), 1595, 1510, 1400, 1335, 1265, 1215, 915, 900 cm<sup>-1</sup>; H NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  6.94–8.04 (m, 15 H, arom and vinylic  $\beta$  to carbonyl), 6.22 (d, *J* = 10.0 Hz, 1 H, vinylic  $\alpha$  to carbonyl), 3.16 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>C=O), 2.44 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>C=O); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  212.713 (C=O), 138.625, 134.209, 36.361, 32.140, 28.244; UV (95% EtOH) 264 ( $\epsilon$  6667), 276 ( $\epsilon$  9540), 285 ( $\epsilon$  11 839), 294 ( $\epsilon$  11 034), 316 nm ( $\epsilon$  3793); MS, *m/e* 348.1514 (calcd for C<sub>26</sub>H<sub>20</sub>O, *m/e* 348.1513).

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.73; H, 5.92.

**Exploratory Direct Photolysis of 4,4-Di( $\alpha$ -naphthyl)cyclohexenone.** Photolysis was carried out by dissolving 215 mg (0.62 mmol) of 4,4-di( $\alpha$ -naphthyl)cyclohexenone in 200 mL of dry photograde benzene.<sup>36</sup> Purified nitrogen<sup>37</sup> was passed through the solution for 1 h before and during the photolysis. The light source used was a 450-W Hanovia medium-pressure mercury lamp equipped with a 2-mm Pyrex filter, all in an immersion well. The photolysis was complete in 12 min. Concentration in vacuo yielded 260 mg of a light yellow oil. Separation of the photoproduct mixture was performed by using column chromatography on a 0.75 m  $\times$  2 cm silica gel column eluting as follows: 1, 5% ether/hexane, 500 mL, nil; 2, 10% ether/hexane, 250 mL, 112 mg (52%) of *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one; 3, 15% ether/hexane, 500 mL, 91 mg (42%) of 3,4-di( $\alpha$ -naphthyl)cyclohex-2-enone.

The *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 105 mg (49%), mp 151–152.5 °C. The spectral data were the following: IR (CHCl<sub>3</sub>) 3020, 1720 (C=O), 1600, 1520, 1420 cm<sup>-1</sup>; H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  6.80–9.00 (m, 14 H, arom), 3.56 (ab, *J* = 9.56 Hz, 1 H, cyclopropyl), 2.91 (ab, *J* = 9.56 Hz, 1 H, cyclopropyl), 2.59 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>C=O), 2.18 (dd, *J* = 9.45, 18.38 Hz, 1 H, exo H), 1.12 (dd, *J* = 9.45, 18.38 Hz, 1 H, endo H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  212.71 (C=O), 43.18, 42.27, 36.36, 32.14, 28.24; UV (95% ethanol) 264 ( $\epsilon$  8762), 273 ( $\epsilon$  14 290), 285 ( $\epsilon$  18 770), 296 ( $\epsilon$  15 540), 314 nm ( $\epsilon$  2796); MS, *m/e* 348.1507 (calcd for C<sub>26</sub>H<sub>20</sub>O, *m/e* 348.1513).

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.71; H, 5.85.

The 3,4-di( $\alpha$ -naphthyl)cyclohex-2-enone was recrystallized from 95% ethanol to give 85 mg (40%), mp 152–153 °C. The spectral data were the following: IR (CHCl<sub>3</sub>) 3050, 3005, 2960, 2920, 2860, 1675 (C=O), 1600, 1515, 1455, 1400, 1350, 1335, 1235, 1165, 1030, 980, 920 cm<sup>-1</sup>;

(32) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratory, Inc., Knoxville, TE. All reactions were run under dry nitrogen. *tert*-Butyl alcohol utilized for irradiation experiments was distilled from calcium hydride. THF was purified by storage over KOH, followed by successive distillation under a nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. 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 quartz columns permitting monitoring by a hand-held UV lamp. Neutral workup refers to dilution with ether, washing with water and brine, drying over anhydrous magnesium sulfate or sodium sulfate, filtering, and concentrating in vacuo. Acidic workup added an initial 10% HCl wash after dilution. Basic workup added an initial saturated NaHCO<sub>3</sub> wash after dilution. Acidic–basic workup used both acid and base washes after dilution.

(33) Reif, D. J.; House, H. O. "Organic Syntheses"; J. Wiley and Sons: New York, 1963; Collect. Vol. IV, pp 860–862.

(34) Drefahl, G.; Lorenz, D.; Schnitt, G. *J. Prakt. Chem.* **1964**, *295*, 143–148.

(35) Reif, D. J.; House, H. O. "Organic Syntheses"; J. Wiley and Sons: New York, 1963; Collect. Vol. IV, pp 375–377.

(36) Benzene for photolysis was purified by repeated washing with acidic saturated potassium permanganate solution followed by repeated washing with concentrated sulfuric acid, water, and brine, drying over magnesium sulfate, and distilling through a 30-cm column of metal helices from calcium hydride.

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



H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09–8.25 (m, 14 H, arom), 6.57 (s, 1 H, vinylic), 5.17 (m, 1 H, CHAr), 2.25–2.97 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ); UV (95% ethanol) 264 ( $\epsilon$  7751), 274 ( $\epsilon$  11705), 296 ( $\epsilon$  10282), 316 nm ( $\epsilon$  3796); MS,  $m/e$  348.1514 (calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ ,  $m/e$  348.1513).

Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ : C, 89.62; H, 5.79. Found: C, 89.43; H, 6.03.

**Exploratory Xanthone-Sensitized Photolysis of 4,4-Di( $\alpha$ -naphthyl)cyclohex-2-en-1-one.** A solution of 250 mg (0.72 mmol) of 4,4-di( $\alpha$ -naphthyl)cyclohex-2-enone and 7.8 g (40 mmol) of xanthone in 400 mL of photograde benzene<sup>36</sup> was purged with purified nitrogen<sup>37</sup> for 1 h and irradiated for 10 min with continuous purging with use of a Hanovia 450-W, medium-pressure mercury lamp through a 2-mm Pyrex filter. The photolysate was concentrated in vacuo to give 8.3 g of a slightly yellow solid which was chromatographed on a 2.5 cm  $\times$  90 cm silica gel column, eluting as follows: 1, 5% ether/hexane, 2000 mL, 7.5 g of xanthone; 2, 5% ether/hexane, 250 mL, 117 mg (47%) of *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one; 3, 10% ether/hexane, 500 mL, nil; 4, 15% ether/hexane, 250 mL, 120 mg (48%) of 3,4-di( $\alpha$ -naphthyl)cyclohexenone.

The *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 105 mg of colorless prisms, mp 151–152.5 °C.

The 3,4-di( $\alpha$ -naphthyl)cyclohex-2-enone was recrystallized from 95% ethanol to give 110 mg of colorless prisms, mp 152–153 °C. The spectral data were identical in all respects with that obtained in the direct photolysis of 4,4-di( $\alpha$ -naphthyl)cyclohexenone (vide supra).

**Exploratory Thioxanthone-Sensitized Photolysis of 4,4-Di( $\alpha$ -naphthyl)cyclohexenone.** A solution of 250 mg (0.72 mmol) of 4,4-di( $\alpha$ -naphthyl)cyclohexenone and 9.5 g (50 mmol) of thioxanthone in 450 mL of photograde benzene<sup>36</sup> was purged with purified nitrogen<sup>37</sup> for 1 h and irradiated for 13 min with continuous purging with use of a Hanovia 450-W, medium-pressure mercury lamp through a 2-mm Pyrex filter. The photolysate was concentrated in vacuo to give 10.0 g of a light yellow solid. Column chromatography on a 2 cm  $\times$  75 cm silica gel column gave the following fractions: 1, 5% ether/hexane, 2500 mL, 9.3 g of thioxanthone; 2, 5% ether/hexane, 250 mL, nil; 3, 10% ether/hexane, 500 mL, 122 mg of *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one; 4, 10% ether/hexane, 300 mL, nil; 5, 15% ether/hexane, 500 mL, 112 mg of 3,4-di( $\alpha$ -naphthyl)cyclohexenone.

The *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 115 mg (46%) of colorless crystals, mp 150.5–152 °C.

The 3,4-di( $\alpha$ -naphthyl)cyclohexenone was recrystallized from 95% ethanol to give 108 mg (43%) of colorless crystals, mp 152–153 °C. The spectral data were identical in all respects with that obtained in the direct photolysis of 4,4-di( $\alpha$ -naphthyl)cyclohexenone (vide supra).

**4-( $\alpha$ -Naphthyl)cyclohexan-1,3-dione.** To a slurry of 5.6 g (50.0 mmol) of potassium *tert*-butoxide in 900 mL of dry ether was added at 0 °C 10.0 g (50.0 mmol) of methyl 2-( $\alpha$ -naphthyl)acetate in 100 mL of dry ether. After the mixture was stirred for 10 min, a catalytic amount of dicyclohexyl-18-crown-6 (0.25 g) was added. A solution of 2.50 mL (30.0 mmol) of methyl vinyl ketone in 250 mL of dry ether was added dropwise via syringe pump at the rate of 50 mL/h. The mixture was allowed to slowly warm to room temperature overnight and then refluxed for 72 h. The mixture was cooled to room temperature when 200 mL of water was added and stirred for 10 min. The aqueous layer was separated, acidified to Congo red, saturated with ammonium sulfate, extracted three times with ether, dried over magnesium sulfate, filtered, and concentrated in vacuo to give 5.2 g of a light yellow oil. Recrystallization from dioxane gave 4.5 g (38%) of 4-( $\alpha$ -naphthyl)cyclohexan-1,3-dione, mp 202–204 °C dec (sealed tube). The spectral data were the following: IR (KBr) 3400, 3030, 2940, 2840, 1645, 1590, 1520, 1405, 1390, 1330, 1300, 1270, 1240, 1220, 1180, 1145, 1115, 1075, 1035, 1020, 995, 955, 840, 790  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{Me}_2\text{SO}-d_6$ )  $\delta$  7.0–7.88 (m, 7 H, arom), 5.36 (s, 0.62 H, vinylic), 4.26 (m, 1 H, CH), 3.44 (s, 0.74 H,  $\text{O}=\text{CCH}_2\text{C}=\text{O}$ ), 3.32 (m, 0.62 H, OH), 2.24 (m, 4 H,  $\text{CH}_2\text{CH}_2$ ); MS,  $m/e$  238.0993 (calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ ,  $m/e$  238.0993).

Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ : C, 80.65; H, 5.92. Found: C, 80.53; H, 6.03.

Analysis by H NMR showed that in  $\text{Me}_2\text{SO}$  solution, 60% existed in the enol form and 40% existed in the keto form. In the solid state (by IR), the compound existed only in the enol form.

**4-Methoxy-1-( $\alpha$ -naphthyl)cyclohex-3-en-2-one and 4-( $\alpha$ -Naphthyl)-3-methoxycyclohex-2-en-1-one.** To a solution of 1.0 g (4.2 mmol) of 4-( $\alpha$ -naphthyl)cyclohexan-1,3-dione in 50 mL of dry MeOH was added 0.25 g (1.3 mmol) of *p*-toluenesulfonic acid. After the solution was refluxed for 4 h, basic workup<sup>32</sup> afforded 1.2 g of an orange gum. This was adsorbed onto alumina and chromatographed on an alumina column 1.5 m  $\times$  2.5 cm eluting with 20% ethyl acetate/hexane, collecting 50-mL fractions. Fractions 1–10 contained 0.40 g of a yellow oil which was recrystallized from ether/hexane to give 0.35 g (33%) of 4-methoxy-

1-( $\alpha$ -naphthyl)cyclohex-3-en-2-one, mp 115–117 °C. Fractions 15–30 contained 0.31 g of a light yellow oil which was recrystallized from methylene chloride/hexane to give 0.29 g (27%) of 4-( $\alpha$ -naphthyl)-3-methoxycyclohex-2-enone, mp 107–109 °C.

The 4-( $\alpha$ -naphthyl)-3-methoxycyclohex-2-en-1-one could be conveniently hydrolyzed back to 4-( $\alpha$ -naphthyl)cyclohexane-1,3-dione by treatment of a THF solution of the enone in 10% hydrochloric acid for 24 h. Workup in the dione experimental (vide supra) was followed. The spectral data for 4-methoxy-1-( $\alpha$ -naphthyl)cyclohex-3-en-1-one were the following: IR ( $\text{CHCl}_3$ ) 3045, 2985, 2930, 1640 ( $\text{C}=\text{O}$ ), 1600, 1502, 1450, 1420, 1315, 1263, 1145, 1178, 1150, 1070, 1000, 970, 915, 840, 820, 740, 650  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–7.80 (m, 7 H, arom), 5.48 (s, 1 H, vinylic), 4.12 (t,  $J = 7.0$  Hz, 1 H, CHAr), 3.60 (s, 3 H,  $\text{OCH}_3$ ), 2.28 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ); MS,  $m/e$  252.1151 (calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_2$ ,  $m/e$  252.1151).

Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_2$ : C, 80.93; H, 6.39. Found: C, 81.09; H, 6.50.

The spectral data for 4-( $\alpha$ -naphthyl)-3-methoxycyclohex-2-enone were the following: IR ( $\text{CHCl}_3$ ) 3000, 2930, 1640 ( $\text{C}=\text{O}$ ), 1600, 1510, 1450, 1215  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–7.96 (m, 7 H, arom), 5.68 (s, 1 H, vinylic), 4.48 (m, 1 H, CHAr), 3.64 (s, 3 H,  $\text{OCH}_3$ ), 2.35 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ); MS,  $m/e$  252.1149 (calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_2$ ,  $m/e$  252.1151).

Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_2$ : C, 80.93; H, 6.39. Found: C, 81.12; H, 6.62.

**3,4-Di( $\alpha$ -naphthyl)cyclohex-2-en-1-one.** To a solution of 0.933 mL (1.40 mmol) of 1.5 M *n*-butyllithium in 10 mL of dry THF was added 0.194 mL (1.39 mmol) of 1-bromonaphthalene at  $-78$  °C. After 15 min, 177 mg (0.703 mmol) of 4-methoxy-1-( $\alpha$ -naphthyl)cyclohex-3-en-2-one in 10 mL of dry ether was added dropwise with stirring. This was allowed to stir at this temperature for 1 h when it was warmed to room temperature. The solution was quenched by adding 10 mL of 10% HCl solution to it along with 10 mL of ether and was stirred for 3.5 h. Basic workup<sup>32</sup> gave 300 mg of a brown oil which was chromatographed by first adsorbing the crude product on silica gel and eluting first with 5% ether/hexane giving naphthalene as the first compound followed by 20% ether/hexane giving 51 mg (21%) of pure 3,4-di( $\alpha$ -naphthyl)cyclohex-2-en-1-one which was recrystallized from 95% ethanol to give 48 mg (20%) of pure enone, mp 152–153 °C. The spectral data matched that of the photoproduct (vide supra).

**Lithium-Liquid Ammonia Reduction of *trans*-5,6-Di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one.** To a solution of 300 mg (0.750 mmol) of *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one in 5 mL of dry THF and 50 mL of distilled ammonia (Na) was added 13.0 mg (1.85 mmol) of freshly cut lithium. The blue color persisted, then turned brown, and 100 mg of ammonium chloride was added. After the ammonia evaporated, neutral workup<sup>32</sup> gave 310 mg of a yellow-brown oil. The oil was adsorbed onto silica gel and chromatographed on a 2 m  $\times$  3 cm silica gel column as follows: 1, 5% methylene chloride/hexane, 500 mL, nil; 2, 10% methylene chloride/hexane, 250 mL, nil; 3, 15% methylene chloride/hexane, 500 mL, 112 mg of starting material; 4, 20% methylene chloride/hexane, 500 mL, 51 mg of a 1:1 mixture of starting material and reduction product; 5, 25% methylene chloride/hexane, 1000 mL, 115 mg of reduction product identified as 3-( $\alpha$ -naphthyl)-2-( $\alpha$ -naphthylmethyl)cyclopentanone. Recrystallization from ether/hexane gave 110 mg (41%), mp 138–139.5 °C. The spectral data were the following: IR ( $\text{CHCl}_3$ ) 3010, 2960, 2880, 1740 ( $\text{C}=\text{O}$ ), 1605, 1520, 1460, 1405, 1340, 1270, 1235, 1150, 1070, 1025, 940, 920, 875, 800  $\text{cm}^{-1}$ ; H NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80–7.80 (m, 14 H, arom), 3.75 (m, 3 H,  $\text{CHCH}_2\text{Ar}$ ), 3.15 (ddd,  $J = 3.1, 6.8, 8.1$  Hz, 1 H, CHAr), 2.45 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ), 1.80 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  216.466 ( $\text{C}=\text{O}$ ), 55.373, 43.338, 37.761, 31.909, 30.088; MS,  $m/e$  350.1670 (calcd for  $\text{C}_{26}\text{H}_{22}\text{O}$ ,  $m/e$  350.1671).

Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{O}$ : C, 89.11; H, 6.33. Found: C, 89.02; H, 6.49.

**Epimerization of *cis*-2-( $\alpha$ -naphthylmethyl)-3- $\alpha$ -naphthylcyclopentanone.** To a solution of 116 mg (0.3 mmol) of *cis*-2-( $\alpha$ -naphthylmethyl)-3- $\alpha$ -naphthylcyclopentanone in 10 mL of absolute ethanol was added 0.2 mL of 1.8 M sodium ethoxide (prepared by dissolving 2.1 g of Na in 50 mL of absolute ethanol). This was allowed to stir for 3 h. The solution was poured into saturated ammonium chloride, separated, dried over sodium sulfate, filtered, and concentrated in vacuo to give 104 mg of a yellow solid which was recrystallized from ethanol to give 98 mg of *trans*-2-( $\alpha$ -naphthylmethyl)-3- $\alpha$ -naphthylcyclopentanone, mp 126–127 °C. The spectral data were the following: IR ( $\text{CCl}_4$ ) 3010, 2960, 2880, 1739 ( $\text{C}=\text{O}$ ), 1605, 1520, 1460, 1405, 1340, 1270, 1235, 1150, 1070, 940, 920, 875  $\text{cm}^{-1}$ ; H NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80–7.80 (m, 14 H, arom), 3.75 (m, 3 H,  $\text{CHCH}_2\text{Ar}$ ), 3.15 (ddd,  $J = 4.9, 7.0, 7.2$  Hz, 1 H, CHAr), 2.45 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ), 1.80 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  215.476 ( $\text{C}=\text{O}$ ), 54.360, 42.317, 36.682, 30.882, 29.003; MS,  $m/e$  350.1669 (calcd for  $\text{C}_{26}\text{H}_{22}\text{O}$ ,  $m/e$  350.1671).

**cis-3-( $\alpha$ -Naphthyl)-2-(phenylthio)cyclopentan-1-one.** To a solution of 36.0 mL (49.6 mmol) of 1.5 M *n*-BuLi in 80 mL of dry THF at  $-78^\circ\text{C}$  was added dropwise 6.9 mL (49.6 mmol) of 1-bromonaphthalene. After the mixture was stirred for 10 min at this temperature, the 1-lithio-naphthalene formed was transferred via syringe to a flask containing 9.67 g (24.8 mmol) of tetrakis(tributylphosphine)copper(I) iodide in 250 mL of dry ether at  $-78^\circ\text{C}$ . This was allowed to stir for 30 min when 1.19 g (6.20 mmol) of 2-(phenylthio)cyclopentan-2-en-1-one<sup>38</sup> was added dropwise in 5 mL of dry THF to the cuprate solution. After 10 min of stirring, the solution turned from clear to green orange to cloudy yellow. The solution was allowed to stir for 1 h more. The solution was warmed to  $0^\circ\text{C}$  and was poured into a saturated ammonium chloride solution. Ether was added and the organic layer was washed twice more with saturated ammonium chloride solution. The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to give 7.0 g of a light yellow oil which was adsorbed on silica gel. This was chromatographed on a 2 m  $\times$  3 cm silica gel column as follows: 1, 5% ether/hexane, 500 mL, 4.5 g of tributylphosphine-naphthalene mixture; 2, 15% ether/hexane, 1000 mL, 1.89 g (95%) of *cis*-3-( $\alpha$ -naphthyl)-2-(phenylthio)cyclopentanone as a light yellow oil. The spectral data were the following: IR (neat) 3045, 2960, 2870, 1745 (C=O), 1600, 1580, 1545, 1510, 1480, 1440, 1400, 1380, 1365, 1280, 1215, 1145, 1085, 1025, 915, 865, 800, 775, 745, 695  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  6.70–8.20 (m, 12 H, arom), 3.95 (m, 1 H, CHAr), 3.75 (d,  $J = 4.0$  Hz, 1 H, CHSPH), 2.40 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  212.323 (C=O), 58.630, 43.392, 35.995, 35.553, 28.376; MS,  $m/e$  318.1071 (calcd for  $\text{C}_{21}\text{H}_{18}\text{OS}$ ,  $m/e$  318.1078).

Anal. Calcd for  $\text{C}_{21}\text{H}_{18}\text{OS}$ : C, 79.21; H, 5.67. Found: C, 79.39; H, 5.88.

**3-( $\alpha$ -Naphthyl)-2-(phenylthio)-2-( $\alpha$ -naphthylmethyl)cyclopentanone.** To a slurry of 0.121 g (2.69 mmol) of 50% sodium hydride in mineral oil (which had been washed twice with pentane to remove the mineral oil) in 10 mL of glyme at  $0^\circ\text{C}$  was added a drop of ethanol. Then 0.729 g (2.29 mmol) of 3-( $\alpha$ -naphthyl)-2-(phenylthio)cyclopentanone in 5 mL of glyme was added dropwise to the stirred solution. Then, after 30 min, 0.875 g (3.27 mmol) of 1-(iodomethyl)naphthalene in 5 mL of glyme was added dropwise. The reaction mixture was allowed to stir for 2 h and then was allowed to slowly warm to room temperature and was stirred for 10 h at this temperature. The solution was poured into saturated ammonium chloride and basic workup<sup>32</sup> gave 1.0 g of a dark brown oil. This was adsorbed onto silica gel and chromatographed on a 60 cm  $\times$  3 cm silica gel column as follows: 1, hexane, 500 mL, 0.20 g of naphthyl hydrocarbon; 2, 10% ether/hexane, 500 mL, nil; 3, 15% ether/hexane, 500 mL, alkylation product, 0.50 g; 4, 20% ether/hexane, 500 mL, 0.30 g of an unknown cyclopentanone which was not further characterized. The alkylation product, 3-( $\alpha$ -naphthyl)-2-(phenylthio)-2-( $\alpha$ -naphthylmethyl)cyclopentanone, was recrystallized from chloroform/hexane to give 0.48 g (47%), mp  $206$ – $207^\circ\text{C}$ . The spectral data were the following: IR ( $\text{CHCl}_3$ ) 3040, 2980, 2930, 1720 (C=O), 1590, 1500, 1430, 1390, 1140, 1130, 1070, 1020, 965, 795, 685  $\text{cm}^{-1}$ ; H NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55–8.00 (m, 19 H, arom), 4.25 (dd,  $J = 6.6, 12.5$  Hz, 1 H, CHAr), 3.61 (ab,  $J = 15.8$  Hz, 2 H,  $\text{CH}_2\text{Ar}$ ), 2.10–3.05 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.361 (C=O), 67.463, 43.724, 36.216, 34.339, 26.554; MS,  $m/e$  458.1695 (calcd for  $\text{C}_{32}\text{H}_{26}\text{OS}$ ,  $m/e$  458.1698).

Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{OS}$ : C, 83.81; H, 5.41. Found: C, 84.05; H, 5.98.

**3-( $\alpha$ -Naphthyl)-2-( $\alpha$ -naphthylmethyl)cyclopentanone.**<sup>39</sup> To a solution of 0.227 g (1.60 mmol) of anhydrous disodium hydrogen phosphate in 10 mL of dry methanol was added 0.191 g (0.400 mmol) of 3-( $\alpha$ -naphthyl)-2-(phenylthio)-2-( $\alpha$ -naphthylmethyl)cyclopentanone in 5 mL of dry THF. To this solution was added 0.600 g of 6% sodium amalgam at room temperature. The solution was stirred 2 h at which time the sodium amalgam had turned to a mercury droplet. After the solution was filtered through a glass wool plug, neutral workup<sup>32</sup> gave 130 mg of a yellow oil. Adsorption onto silica gel followed by chromatography on a 50 cm  $\times$  2 cm silica gel column eluting with 10% methylene chloride/hexane gave after recrystallization from ether/hexane 117 mg (83%) of 3-( $\alpha$ -naphthyl)-2-( $\alpha$ -naphthylmethyl)cyclopentanone, mp  $138$ – $139.5^\circ\text{C}$ . The spectral data matched that of the product obtained from the lithium-liquid ammonia reduction of *trans*-5,6-di( $\alpha$ -naphthyl)bicyclo[3.1.0]hexan-2-one (vide supra).

**cis-1,2-Di( $\beta$ -naphthyl)oxirane.** To a slurry of 1.40 g (5.00 mmol) of *cis*-1,2-di( $\beta$ -naphthyl)ethylene and 1.54 g of anhydrous sodium carbonate in 15 mL of dry methylene chloride was added dropwise with stirring 53

mg of sodium acetate trihydrate dissolved in 0.940 g (5.00 mmol) of 40% peracetic acid. This mixture was allowed to stir for 48 h. After complete reaction, the reaction mixture was filtered by aspirator suction. The filter cake was washed several times with methylene chloride until the filter cake or the washings were colorless. The solvent was removed in vacuo to give 1.3 g of an orange oil which was recrystallized from methanol to give 0.932 g (63%) of *cis*-1,2-di( $\beta$ -naphthyl)oxirane, mp  $108.5$ – $109^\circ\text{C}$ . The spectral data were the following: IR ( $\text{CHCl}_3$ ) 3050, 3005, 1640, 1610, 1515, 1480, 1415, 1370, 1340, 1280, 1240, 1170, 1160, 1135, 1055, 1025, 975, 960, 910, 870, 830, 690, 660  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.88 (m, 14 H, arom), 4.56 (s, 2 H, epoxy);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  60.126; MS,  $m/e$  296.1200 (calcd for  $\text{C}_{22}\text{H}_{16}\text{O}$ ,  $m/e$  296.1200).

Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{O}$ : C, 89.14; H, 5.44. Found: C, 88.90; H, 5.61.

**2,2-Di( $\beta$ -naphthyl)acetaldehyde.** To a solution of 11.0 g (37.2 mmol) of *cis*-1,2-di( $\beta$ -naphthyl)oxirane in 110 mL of dry benzene in a separatory funnel was added 2.42 mL (19.6 mmol) of boron trifluoride etherate. This mixture was allowed to stand after being shaken for 1 min when neutral workup<sup>32</sup> gave 10.2 g of a pale cream-colored oil. The solid was adsorbed onto silica gel and placed on a 1 m  $\times$  2 cm silica gel column. The column was eluted with 10% ether/hexane to give one 500-mL fraction containing 8.9 g of a light yellow solid, mp  $147$ – $160^\circ\text{C}$ . The solid was recrystallized from methylene chloride/hexane to give 8.5 g (77%) of 2,2-di( $\beta$ -naphthyl)acetaldehyde, mp  $163$ – $164^\circ\text{C}$ . The spectral data were the following: IR ( $\text{CHCl}_3$ ) 3045, 2960, 2920, 2840, 1725 (C=O), 1650, 1630, 1600, 1505, 1470, 1355, 1290, 1270, 1170, 1130, 1020, 950, 900, 860, 820  $\text{cm}^{-1}$ ; H NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  10.12 (d,  $J = 2$  Hz, 1 H,  $\text{CHCHO}$ ), 7.28–7.96 (m, 14 H, arom), 5.24 (d,  $J = 2$  Hz, 1 H,  $\text{CHCHO}$ ); MS,  $m/e$  296.1200 (calcd for  $\text{C}_{22}\text{H}_{16}\text{O}$ ,  $m/e$  296.1200).

Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{O}$ : C, 89.14; H, 5.44. Found: C, 88.87; H, 5.62.

**4,4-Di( $\beta$ -naphthyl)cyclohex-2-en-1-one.** To a solution of 2.50 g (8.40 mmol) of 2,2-di( $\beta$ -naphthyl)acetaldehyde in 42 mL of dry THF was added at  $0^\circ\text{C}$  dropwise with stirring 0.87 mL (2.60 mmol) of 3.0 N KOH in absolute ethanol. This solution was prepared 1 week prior to reaction since it affords higher yields of enone. This mixture was allowed to stir for 10 min when 1.01 mL (9.12 mmol) of methyl vinyl ketone was added dropwise with stirring via syringe pump adding at the rate of 0.5 mL/h. The solution was allowed to warm slowly to room temperature over a 12-h period when it was heated to reflux and allowed to stir at this temperature for 48 h. After the solution was cooled to room temperature, acidic-basic workup<sup>32</sup> gave 3.0 g of a reddish brown oil. The oil was adsorbed onto silica gel and chromatographed on a silica gel column 0.5 m  $\times$  3 cm as follows: 1, 5% methylene chloride/hexane, 500 mL, nil; 2, 10% methylene chloride/hexane, 500 mL, nil; 3, 20% methylene chloride/hexane, 1000 mL, nil; 4, 20% methylene chloride/hexane, 500 mL, 80 mg, unknown not further characterized; 5, 25% methylene chloride/hexane, 1000 mL, 180 mg, unknown not further characterized; 6, 30% methylene chloride/hexane, 100 mL, nil; 7, 25% ether/hexane, 500 mL, nil; 8, 25% ether/hexane, 500 mL, 275 mg of enone product. This was recrystallized from carbon tetrachloride/hexane to give 270 mg (20%) of 4,4-di( $\beta$ -naphthyl)cyclohexenone, mp  $104$ – $105^\circ\text{C}$ . The spectral data were the following: IR ( $\text{CHCl}_3$ ) 3070, 2970, 2940, 2870, 1700 (C=O), 1640, 1610, 1520, 1470, 1400, 1285, 1210, 1140, 1030, 965, 925, 870  $\text{cm}^{-1}$ ; H NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20–7.90 (m, 15 H, arom and  $\beta$  vinylic), 6.33 (d,  $J = 11.0$  Hz, 1 H, vinylic), 2.92 (t,  $J = 6.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ), 2.49 (t,  $J = 6.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ ); UV (95% ethanol) 266 ( $\epsilon$  15 660), 275 ( $\epsilon$  13 630), 287 ( $\epsilon$  8 121), 305 ( $\epsilon$  1740), 320 ( $\epsilon$  870); MS,  $m/e$  348.1514 (calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ ,  $m/e$  348.1513).

Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{O}$ : C, 89.62; H, 5.79. Found: C, 89.33; H, 6.05.

**Exploratory Direct Photolysis of 4,4-Di( $\beta$ -naphthyl)cyclohex-2-en-1-one.** Photolysis was carried out by dissolving 475 mg (1.36 mmol) of 4,4-di( $\beta$ -naphthyl)cyclohexenone in 700 mL of dry photolabile benzene.<sup>36</sup> Purified nitrogen<sup>37</sup> was passed through the solution 1 h prior to and during photolysis. The light source used was a 450-W Hanovia medium pressure mercury lamp equipped with a 2-mm Pyrex filter, all in an immersion well. The photolysis was completed in 2 h and 40 min. The solution was concentrated in vacuo to yield 500 mg of a light yellow oil. Separation of the photoproduct mixture was performed by adsorption of the crude photolysate on silica gel and chromatography on a 1.5 m  $\times$  2 cm silica gel column as follows: 1, hexane, 500 mL, nil; 2, 5% ether/hexane, 1000 mL, nil; 3, 10% ether/hexane, 500 mL, nil; 4, 10% ether/hexane, 1000 mL, 216 mg (45%) of *trans*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one; 5, 10% ether/hexane, 1000 mL, 135 mg (28%) of 4,4-di( $\beta$ -naphthyl)cyclohexenone; 6, 15% ether/hexane, 1000 mL, 94 mg (20%) of *cis*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one.

The *trans*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 210 mg (44%), mp  $144.5$ – $146^\circ\text{C}$ . The

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spectral data were the following: IR (CCl<sub>4</sub>) 3050, 2960, 2930, 2850, 1730 (C=O), 1640, 1605, 1510, 1460, 1415, 1185, 1170, 1075, 955, 915, 900, 865 cm<sup>-1</sup>; H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.40–7.95 (m, 14 H, arom), 3.35 (ab, *J* = 10.00 Hz, 1 H, cyclopropyl), 2.85 (ab, *J* = 10.00 Hz, 1 H, cyclopropyl (C=O)), 2.55 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>C=O), 2.15 (m, 1 H, *exo*-CHC=O), 1.15 (m, 1 H, *endo*-CHC=O); UV (95% ethanol) 268 (ε 18 660), 276 (ε 16 641), 288 (ε 10 590); 305 nm (ε 2521); MS, *m/e* 348.1515 (calcd for C<sub>26</sub>H<sub>20</sub>O, *m/e* 348.1513).

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.34; H, 5.88.

The *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 85 mg (18%), mp 187–188.5 °C. The spectral data were the following: IR (CCl<sub>4</sub>) 3045, 2920, 2840, 1730 (C=O), 1630, 1600, 1510, 1230, 1165, 1130, 910, 890, 860 cm<sup>-1</sup>; H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.80–7.95 (m, 14 H, arom), 3.05 (ab, *J* = 4.00 Hz, 1 H, cyclopropyl), 2.90 (ab, *J* = 4.00 Hz, 1 H, cyclopropyl C=O), 2.30–2.80 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>C=O); UV (95% ethanol) 269 (ε 19 191), 278 (ε 17 656), 291 (ε 11 771), 309 nm (ε 4094); MS, *m/e* 348.1515 (calcd for C<sub>26</sub>H<sub>20</sub>O, *m/e* 348.1513).

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.85; H, 5.63.

**Exploratory Xanthone-Sensitized Photolysis of 4,4-Di(β-naphthyl)cyclohex-2-en-1-one.** A solution of 150 mg (0.43 mmol) of 4,4-di(β-naphthyl)cyclohexenone and 4.9 g (25 mmol) of xanthone in 250 mL of photograde benzene<sup>36</sup> was purged with purified nitrogen<sup>35</sup> for 1 h and irradiated for 15 min with continuous purging with a Hanovia 450-W medium pressure mercury lamp through a 2-mm Pyrex filter. The photolysate was concentrated in vacuo to give 5.1 g of a light yellow solid. Column chromatography on a 2.5 cm × 1 m silica gel column was performed as follows: 1, 5% ether/hexane, 2000 mL, 4.8 g of xanthone; 2, 5% ether/hexane, 500 mL, nil; 3, 10% ether/hexane, 500 mL, 91 mg of *trans*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one; 4, 10% ether/hexane, 500 mL, nil; 5, 15% ether/hexane, 52 mg of *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one.

The *trans*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 85 mg (57%) of colorless crystals, mp 144.5–146 °C.

The *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one was recrystallized from 95% ethanol to give 48 mg (32%) of colorless prisms, mp 187–188 °C. The spectral data were identical in all respects with that obtained from the direct photolysis of 4,4-di(β-naphthyl)cyclohexenone (*vide supra*).

**Exploratory Thioxanthone-Sensitized Photolysis of 4,4-Di(β-naphthyl)cyclohex-2-enone.** A solution of 125 mg of 4,4-di(β-naphthyl)cyclohex-2-enone and 5.3 g (25 mmol) of thioxanthone in 250 mL of photograde benzene<sup>36</sup> was purged with purified nitrogen<sup>37</sup> for 1 h and irradiated for 12 min with continuous purging with a Hanovia 450-W medium pressure mercury lamp through a 2-mm Pyrex filter. The photolysate was concentrated in vacuo to give 5.5 g of a light yellow solid. Column chromatography on a 2 cm × 80 cm silica gel column gave the following fractions: 1, 5% ether/hexane, 2000 mL, 5.15 g of thioxanthone; 2, 5% ether/hexane, 500 mL, nil; 3, 10% ether/hexane, 250 mL, 82 mg of *trans*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one; 4, 10% ether/hexane, 500 mL, 28 mg of *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one.

The *trans* isomer was recrystallized from 95% ethanol to give 70 mg (56%) of colorless crystals, mp 144.5–146 °C.

The *cis* isomer was recrystallized from 95% ethanol to give 52 mg (42%) of colorless crystals, mp 187–188.5 °C. The spectral data were identical in all respects with the data obtained in the direct photolysis of 4,4-di(β-naphthyl)cyclohexenone (*vide supra*).

**Lithium-Liquid Ammonia Reduction of *trans*-5,6-Di(β-naphthyl)bicyclo[3.1.0]hexan-2-one.** To 45 mL of liquid ammonia (distilled from Na) at -78 °C was added 6.3 mg (0.89 mmol) of freshly cut Li. The solution immediately turned dark blue, and 143 mg (0.36 mmol) of *trans*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one in 10 mL of dry THF was added all at once. The solution was stirred for 10 min, at which point it turned yellow. Then 100 mg of ammonium chloride was added and the ammonia allowed to evaporate. The solid was taken up with ether and water, and neutral workup<sup>32</sup> gave 150 mg of a yellow oil. The oil was adsorbed onto silica gel and chromatographed on a 1 m × 1 cm silica gel column, collecting 10-mL fractions: fractions 1–2, hexane, nil; 3–5, 5% ether/hexane, nil; 6–16, 10% ether/hexane, nil; 17–18, 10% ether/hexane, 26 mg of 3-(β-naphthyl)-3-(β-naphthylmethyl)cyclopentanone; 19–20, 15% ether/hexane, 48 mg of 4,4-di(β-naphthyl)cyclohexenone; 21–22, 15% ether/hexane, nil; 23–27, 20% ether/hexane, 49 mg of *cis*-3,4-di(β-naphthyl)cyclohexanone.

The 3-(β-naphthyl)-3-(β-naphthylmethyl)cyclopentanone was recrystallized from 95% ethanol to give 20 mg (17%), mp 144–145 °C. The spectral data were the following: IR (CHCl<sub>3</sub>) 3040, 2950, 1740 (C=O), 1601, 1510, 1410, 1265, 1135, 910, 855, 730 cm<sup>-1</sup>; H NMR (200 MHz,

CDCl<sub>3</sub>) δ 6.95–7.80 (m, 14 H, arom), 3.95 (ab, *J* = 10.2 Hz, 2 H, 3-CH<sub>2</sub>Ar), 2.35 (ab, *J* = 9.0 Hz, 2 H, CH<sub>2</sub>C=O), 1.75 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>C=O); MS, *m/e* 350.1665 (calcd for C<sub>26</sub>H<sub>22</sub>O, *m/e* 350.1671). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>O: C, 89.11; H, 6.33. Found: C, 89.05; H, 6.24.

The *cis*-3,4-di(β-naphthyl)cyclohexanone was recrystallized from 95% ethanol to give 45 mg (36%), mp 180–181 °C. The spectral data were the following: IR (CHCl<sub>3</sub>) 2950, 2860, 1709 (C=O), 1602, 1505, 1265, 1100, 1020, 895, 860 cm<sup>-1</sup>; H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.10–7.90 (m, 14 H, arom), 4.92 (m, 1 H, 4-CHAr), 4.77 (ddd, *J* = 3.7, 3.7, 12.2 Hz, 1 H, 3-CHAr), 2.30–3.20 (m, 6 H, CH<sub>2</sub>CH<sub>2</sub>C=OCH<sub>2</sub>); MS, *m/e* 350.1672 (calcd for C<sub>26</sub>H<sub>22</sub>O, *m/e* 350.1671).

Anal. Calcd for C<sub>26</sub>H<sub>22</sub>O: C, 89.11; H, 6.33. Found: C, 88.94; H, 6.48.

**Lithium-Liquid Ammonia Reduction of *cis*-5,6-Di(β-naphthyl)bicyclo[3.1.0]hexan-2-one.** To 50 mL of liquid ammonia (distilled from Na) at -78 °C was added 4.8 mg (0.68 mmol) of freshly cut lithium. The solution turned dark blue, and 110 mg (0.32 mmol) of *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one in 5 mL of dry THF was added at one time. The solution turned from blue to light brown over a 10-min period. Then 100 mg of ammonium chloride was added and the ammonia allowed to evaporate. The solid was taken up with ether and water, and neutral workup<sup>32</sup> gave 120 mg of a yellow oil. The oil was adsorbed onto silica gel and chromatographed on a 50 × 1 cm column, collecting 10-mL fractions: fractions 1–10, hexane, nil; 16–20, 10% ether/hexane, 33 mg of 3-(β-naphthyl)-3-(β-naphthylmethyl)cyclopentanone; 21–30, 15% ether/hexane, 65 mg of starting bicyclic ketone. The 3-(β-naphthyl)-3-(β-naphthylmethyl)cyclopentanone was recrystallized from 95% ethanol to give 25 mg (23%) of white crystals, mp 144–145 °C. The spectral data were identical with that obtained in the lithium-liquid ammonia reduction of *trans*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one (*vide supra*).

**3-(β-Naphthylmethyl)-3-(β-naphthyl)cyclopentanone.** To a solution of 1.41 g (58 mmol) of dry Mg in 20 mL of dry ether was added dropwise with stirring by syringe pump at a rate of 6.0 mL/h 13.0 g (58.3 mmol) of β-(bromomethyl)naphthalene in 20 mL of dry ether. The β-(bromomethyl)naphthalene was purified by recrystallization from methanol, followed by sublimation at 50 °C (1 torr). After addition of the halide was complete, the solution was allowed to stir for 3 h to ensure complete formation of the Grignard reagent. The Grignard reagent was then transferred via syringe to another flask which was equipped with a mechanical stirrer. Then 1.21 g (5.8 mmol) of cuprous bromide-dimethyl sulfide complex was slowly added to the solution cooled with an ice bath. This mixture was allowed to stir for 1 h at this temperature when 5.09 g (24.5 mmol) of 3-(β-naphthyl)cyclopent-2-enone<sup>40</sup> in 40 mL of dry THF was added dropwise over a 30-min period. The solution was slowly warmed to room temperature and allowed to stir another 16 h when acidic workup<sup>32</sup> gave 13.5 g of an orange-brown oil. This solid was adsorbed onto silica gel and chromatographed on a 1/2 m × 3 cm silica gel column as follows: 1, 5% ether/hexane, 1000 mL, nil; 2, 10% ether/hexane, 1000 mL, 10.5 g of (β-naph)CH<sub>2</sub>CH<sub>2</sub>(β-naph); 3, 20% ether/hexane, 500 mL, starting material; 4, 20% ether/hexane, 1000 mL, 1.29 g (14%) of 3-(β-naphthylmethyl)-3-(β-naphthyl)cyclopentanone. This was recrystallized from 95% ethanol to give 1.15 g (13%) of white crystals, mp 144–145 °C. The spectral data were identical with that found in the lithium-liquid ammonia reduction of *trans*- and *cis*-5,6-di(β-naphthyl)bicyclo[3.1.0]hexan-2-one (*vide supra*).

**3,4-Di(β-naphthyl)cyclohex-2-enone.** To a solution of 0.342 g (1.15 mmol) of desoxy-β-naphthoin in 6 mL of dry THF at 0 °C was added 0.118 mL (0.29 mmol) of 3.0 N potassium hydroxide in absolute ethanol (which had been in a dark bottle for 5 days). The solution immediately turned dark. This mixture was allowed to stir for 5 min when 0.138 mL (1.14 mmol) of methyl vinyl ketone was added dropwise with stirring. The solution turned from dark green to light brown upon addition of the methyl vinyl ketone. This mixture was allowed to stir at this temperature for 6 h when it slowly warmed to room temperature. The solution was stirred at this temperature for 24 h and then refluxed for 24 h. After the solution was cooled to room temperature, acidic-basic workup<sup>32</sup> gave 500 mg of an orange solid. The solid was adsorbed onto silica gel and chromatographed on a 1/2 m × 3 cm silica gel column eluting with the following fractions: fraction 1, hexane, 500 mL, nil; 2, 5% ether/hexane, 500 mL, nil; 3, 10% ether/hexane, 500 mL, 130 mg of 3,4-di(β-naphthyl)cyclohex-2-enone. The enone was then recrystallized from 95% ethanol to give 118 mg (30%), mp 135–137.5 °C. The spectral data were the following: IR (CHCl<sub>3</sub>) 3045, 3000, 2960, 2910, 2870, 1670 (C=O), 1605, 1450, 1400, 1350, 1340, 980 cm<sup>-1</sup>; H NMR (100 MHz, CDCl<sub>3</sub>) δ 6.95–7.95 (m, 14 H, arom), 6.35 (s, 1 H, vinylic), 4.55 (m, 1 H, CHAr), 2.15–2.78 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>C=O); MS, *m/e* 348.1513 (calcd for C<sub>26</sub>H<sub>20</sub>O, *m/e* 348.1513).

Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.85; H, 5.45.

Table VII. Summary of  $\alpha$ -Naphthyl Quantum Yield Runs

run	light, mEinstein ( $\times 10^3$ )	enone concn, M ( $\times 10^3$ )	additive, M <sup>c</sup>	conversion, %	trans [3.1.0], mmol ( $\times 10^3$ )	3,4-enone, mmol ( $\times 10^3$ )	$\phi$	
							trans	3,4
1D <sup>a</sup>	38.8	5.25		7.0	6.6	8.1	0.169	0.209
2D <sup>a</sup>	4.9	5.70		1.8	1.9	2.2	0.389	0.457
3D <sup>a</sup>	2.4	6.10		0.9	1.0	1.2	0.425	0.500
4D <sup>b</sup>	4.2	6.32		1.5	1.6	2.2	0.382	0.517
5D <sup>b</sup>	6.7	3.82		3.2	2.0	2.9	0.305	0.435
6D <sup>b</sup>	2.1	0.54		5.2	0.50	0.62	0.224	0.295
7S <sup>a</sup>	73.0	5.67	0.10X	8.5	8.8	10.5	0.121	0.144
8S <sup>a</sup>	14.8	9.42	0.05X	3.6	5.4	8.2	0.367	0.553
9S <sup>a</sup>	7.7	5.27	0.05X	3.5	3.1	4.3	0.405	0.561
10S <sup>b</sup>	2.2	3.44	0.05X	1.6	1.0	1.2	0.459	0.532
11S <sup>b</sup>	3.6	2.65	0.05X	3.3	1.6	1.9	0.432	0.529
12S <sup>b</sup>	22.6	6.10	0.10X	8.4	8.9	11.6	0.394	0.512
13S <sup>a</sup>	3.6	3.33	0.03T	2.4	1.2	2.0	0.332	0.565
14S <sup>a</sup>	3.0	3.35	0.03T	1.9	1.2	1.5	0.420	0.500
15S <sup>a</sup>	1.5	2.87	0.03T	1.3	0.6	0.9	0.389	0.602
16S <sup>b</sup>	3.7	3.33	0.03T	2.7	1.5	2.1	0.407	0.562
17S <sup>b</sup>	4.0	2.95	0.03T	3.3	1.7	2.2	0.415	0.551
18S <sup>b</sup>	1.7	3.03	0.03T	1.4	0.7	1.0	0.425	0.583
19Q <sup>a</sup>	23.6	2.43	0.02N	8.8	4.0	4.6	0.169	0.194
20Q <sup>a</sup>	14.6	1.20	0.04N	9.3	2.1	2.4	0.143	0.164
21Q <sup>a</sup>	18.1	3.95	0.05N	5.5	3.7	5.0	0.205	0.275
22Q <sup>a</sup>	29.8	2.65	0.05C	6.5	3.0	3.9	0.100	0.130
23Q <sup>a</sup>	23.2	2.18	0.10C	2.0	0.93	0.81	0.040	0.035
24Q <sup>a</sup>	8.5	2.33	0.15C	1.1	0.39	0.64	0.046	0.075
25Q <sup>a</sup>	19.3	2.26	0.08C	6.2	3.0	2.6	0.153	0.136

<sup>a</sup> Photolysis carried out in benzene. <sup>b</sup> Photolysis carried out in *tert*-butyl alcohol. <sup>c</sup> X = xanthone sensitized; T = thioxanthone sensitized; N = di-*tert*-butylnitroxyl quenched; <sup>d</sup> C = cyclohexadiene quenched. <sup>d</sup> The concentrations were adjusted so the photolysate was adsorbing >98% of the light. <sup>e</sup> Direct runs were at 352 nm. Xanthone runs were also at 352 nm. Thioxanthone runs were at 366 nm. Quenched runs were at 313 nm.

Table VIII. Summary of  $\beta$ -Naphthyl Quantum Yield Runs

run	light, mEinstein ( $\times 10^3$ )	enone concn, M ( $\times 10^3$ )	additive <sup>c</sup>	conversion, %	trans [3.1.0], mmol ( $\times 10^3$ )	cis [3.1.0], mmol ( $\times 10^3$ )	$\phi$	
							trans	cis
1D <sup>a</sup>	11.4	2.82		3.4	3.6	0.25	0.315	0.022
2D <sup>a</sup>	19.1	1.75		8.0	4.2	1.4	0.220	0.071
3D <sup>a</sup>	17.0	1.45		6.7	3.5	0.43	0.203	0.025
4D <sup>a</sup>	20.8	1.57		8.7	4.3	1.2	0.205	0.058
5D <sup>b</sup>	21.5	1.47		8.2	4.6	0.22	0.216	0.091
6D <sup>b</sup>	11.0	2.13		4.5	3.5	0.31	0.322	0.031
7D <sup>b</sup>	7.4	3.43		2.3	2.8	0.33	0.372	0.037
8S <sup>a</sup>	19.8	1.62	0.05X	7.6	4.1	0.81	0.205	0.039
9S <sup>a</sup>	9.9	1.99	0.05X	4.0	2.7	0.48	0.275	0.051
10S <sup>a</sup>	5.9	3.08	0.05X	1.9	2.2	0.14	0.370	0.018
11S <sup>b</sup>	20.0	1.91	0.05X	7.9	5.2	0.83	0.261	0.039
12S <sup>b</sup>	9.3	2.00	0.05X	4.2	2.9	0.47	0.315	0.050
13S <sup>b</sup>	6.0	3.10	0.05X	2.0	2.4	0.09	0.392	0.015
14S <sup>a</sup>	14.0	1.98	0.03T	5.8	4.3	0.31	0.305	0.023
15S <sup>a</sup>	5.2	2.63	0.03T	1.9	1.9	0.10	0.371	0.020
16S <sup>a</sup>	10.8	2.16	0.03T	4.1	3.1	0.43	0.286	0.042
17S <sup>b</sup>	3.2	2.36	0.03T	1.4	1.2	0.12	0.390	0.020
18S <sup>b</sup>	7.0	2.27	0.03T	3.0	2.5	0.22	0.352	0.031
19S <sup>b</sup>	13.9	1.95	0.03T	7.1	4.7	0.86	0.339	0.086
20Q <sup>a</sup>	13.8	2.82	0.04N	1.6	1.6	0.20	0.116	0.015
21Q <sup>a</sup>	10.9	2.27	0.02N	2.6	2.1	0.26	0.196	0.024
22Q <sup>a</sup>	7.5	0.98	0.05C	1.9	0.62	0.12	0.082	0.016
23Q <sup>a</sup>	7.9	0.75	0.10C	1.5	0.36	0.08	0.046	0.010
24Q <sup>a</sup>	6.2	0.57	0.13C	1.7	0.32	0.07	0.051	0.011
25Q <sup>a</sup>	6.5	0.94	0.08C	1.2	0.38	0.07	0.058	0.011
26Q <sup>a</sup>	20.5	1.32	0.15C	1.4	0.15	0.23	0.025	0.009

<sup>a</sup> Photolysis carried out in benzene. <sup>b</sup> Photolysis carried out in *tert*-butyl alcohol. <sup>c</sup> X = xanthone sensitized; T = thioxanthone sensitized; N = di-*tert*-butylnitroxyl quenched; <sup>d</sup> C = cyclohexadiene quenched. <sup>d</sup> The concentrations were adjusted so the photolysate was adsorbing >98% of the light. <sup>e</sup> Direct runs were at 313 nm. Xanthone runs were at 252 nm. Thioxanthone runs were at 366 nm. Quenched runs were at 313 nm.

**Lithium-Liquid Ammonia Reduction of 3,4-Di( $\beta$ -naphthyl)cyclohex-2-enone.** To 100 mL of liquid ammonia (distilled from Na) was added 11.0 mg (1.56 mmol) of lithium. A solution of 250 mg (0.72 mmol) of 3,4-di( $\beta$ -naphthyl)cyclohex-2-enone in 25 mL of dry THF was added at once. After the blue solution turned yellow, 100 mg of ammonium chloride was added at once and the ammonia allowed to evaporate. After the liquid was taken up in ether and water, neutral workup<sup>2</sup> afforded 262 mg of a yellow oil. The oil was adsorbed onto silica gel and chromatographed on a 1 m  $\times$  2 cm silica gel column as follows: 1, hexane,

500 mL, nil; 2, 10% ether/hexane, 500 mL, 125 mg of *cis*-3,4-di( $\beta$ -naphthyl)cyclohexanone; 3, 15% ether/hexane, 500 mL, 120 mg of starting enone. The *cis*-3,4-di( $\beta$ -naphthyl)cyclohexanone was recrystallized from 95% ethanol to give 110 mg (44%), mp 180–181 °C. The spectral data matched that of the product derived from the lithium-liquid ammonia reduction of *trans*-5,6-di( $\beta$ -naphthyl)bicyclo[3.1.0]hexan-2-one (vide supra).

**HPLC Analytical Methods.** Analyses were performed on 0.3 cm  $\times$  25 cm  $\times$  5  $\mu$ m spherical silica columns.<sup>41</sup> A 5000-psi (LDC) minipump

equipped with pulse damper was used. All analyses were performed with 10% ethyl acetate in hexane. Monitoring was by UV with modified LDC and ISCO scanners. *p*-Phenylphenacyl chloride was used as the internal standard. Where amounts of products were very different, analyses for the major and for the minor components were carried out in separate injections with the amount of the internal standard being adjusted close to each component analyzed. Integration of the curves was by PDP-11/55 digitization with a Bitpad (Summagraphics Co.) digitizer and appropriate programming; 0.5% reproducibility on any given peak was observed.

**Quantum Yield Determinations.** Quantum yields were determined with use of the microbench apparatus described by us earlier<sup>42</sup> with the entrance slit set at 3.6 mm and the exit slit set at 2.0 mm with a band pass of 15 nm at half-peak height. Light was measured with the electronic actinometer we reported,<sup>43</sup> and all runs were calibrated with ferrioxalate actinometry.<sup>44</sup> Analyses were performed with use of HPLC analysis as described above. In each case, runs were made to varying conversions and the efficiencies extrapolated to 0% conversion. Photolysis mixtures were checked to make certain that light-absorbing impurities had not developed. Sensitizer concentrations were adjusted high enough to effect efficient energy transfer but low enough to preclude singlet transfer. Xanthone and thioxanthone were removed from the photolysates by rapid column chromatography on a 2 cm × 40 cm slurry packed silica gel column eluting first with 5–10% ether/hexane to remove the sensitizer followed by 20–25% ether/hexane to remove the photolysate. Cyclohexadiene was removed by simple concentration in vacuo, and di-*tert*-butyl nitroxide was removed by bulb-to-bulb distillation (45 °C at 0.05 torr). Table VII lists individual  $\alpha$ -naphthyl runs while Table VIII lists individual  $\beta$ -naphthyl runs.

**Emission Measurements.** Phosphorescence and fluorescence measurements were made on an Aminco-Kiers spectrofluorometer-fluorometer equipped with a Hanovia 901C-1, 150-W xenon arc lamp and modified with internal baffles to eliminate scatter interfaced to a PDP 11/55 minicomputer. The fluorescence spectra were obtained at 295 K, and the phosphorescence spectra were obtained at 77 K in methylcyclohexane-isopentane (4:1) glass with the samples being thoroughly degassed immediately before measurements were made. The concentrations were adjusted to give an optical density in the range of 0.5–0.8 to minimize scatter. Self-quenching was shown to be unimportant at these concentrations ( $10^{-4}$  M). The excitation wavelength used in all

cases was 285 nm. The emission spectra were calibrated by use of a low-pressure mercury lamp prior to each run. A naphthalene blank spectrum was run of the same concentration as the enone runs to ascertain the relative intensity of the enone fluorescence compared to naphthalene itself. The intensity of the  $\alpha$ -naphthyl enone fluorescence was found to be 10000 times weaker than naphthalene while the  $\beta$ -naphthyl enone was found to be 1020 times weaker than the naphthalene sample. The 0–0 band in the fluorescence of both  $\alpha$ - and  $\beta$ -naphthyl enones was found to occur at an energy of 89 kcal/mol.

**Molecular Mechanics Calculations.** All molecular mechanical calculations were performed with use of the "TRIBBLE" program package<sup>18c</sup> containing the MMPI<sup>18a,b</sup> molecular mechanics program. Where torsional, stretching, bending, and stretch-bend constants were not available, constants approximating them were employed.

**Quantum Mechanics Calculations.** All quantum mechanical calculations were performed with use of the "MOPAC" program package<sup>30b</sup> containing the MNDO<sup>30a</sup> quantum mechanics program. Geometries were obtained by the use of MMPI<sup>18a,b</sup> in the "TRIBBLE" program package.<sup>18c</sup>

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**Registry No.** 4, 98393-55-6; 5, 98393-68-1; *cis*-6, 13528-49-9; *trans*-6, 13528-48-8; *cis*-7, 81052-73-5; 8, 98585-92-3; 9, 98586-00-6; 10, 98585-93-4; 11, 98585-94-5; 12, 98585-95-6; 13, 98585-89-8; 14, 98586-04-0; 15, 98585-88-7; 16, 98585-96-7; 17, 98585-90-1; 18, 98586-01-7; 19, 98586-02-8; 20, 98585-91-2; 21, 98586-03-9; 23, 98585-98-9; 22, 34780-08-0; 24, 98585-99-0; H<sub>2</sub>C=CHCOCH<sub>3</sub>, 78-94-4; *cis*-1,2-di( $\alpha$ -naphthyl)ethylene, 2633-10-5; *trans*-1,2-di( $\alpha$ -naphthyl)ethylene, 1233-36-9; methyl 2-( $\alpha$ -naphthyl)acetate, 2876-78-0; 1-bromonaphthalene, 90-11-9; *trans*-2-( $\alpha$ -naphthylmethyl)-3- $\alpha$ -naphthylcyclopentanone, 98585-97-8; 1-lithionaphthalene, 14474-59-0; tetrakis(tributylphosphine)copper(I) iodide, 62566-04-5; 1-(iodomethyl)naphthalene, 24471-54-3; *cis*-1,2-di( $\beta$ -naphthyl)ethylene, 2633-08-1;  $\beta$ -(bromomethyl)naphthalene, 939-26-4; 1,2-di( $\beta$ -naphthyl)ethane, 21969-45-9; desoxy- $\beta$ -naphthoin, 98586-05-1.

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