(d, J = 6.5 Hz, 3 H, C21), 0.669 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 452 (M^+, $C_{32}H_{52}O$, 2), 437 (2), 314 (8), 299 (5), 271 (16), 255 (5), 83 (100), 69 (10), 55 (22).

Dimer (74-M): R_f = 0.59 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.323 (s, 6 H, OMe), 1.019 (s, 6 H, C19), 0.884 (d, J = 6.4, 6 H, C21), 0.712 (s, 6 H, C18); low-resolution mass spectrum, m/z (relative intensity) 658 (M^+, $C_{46}H_{74}O_2$, 6), 643 (7), 603 (20), 255 (10), 145 (17), 95 (30), 71 (98), 55 (99), 42 (100).

THF adduct A (75a-M): R_f = 0.33 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.862 (m, 2 H, THF C4), 3.691 (q, J = 7.4 Hz, 1 H, THF C2), 3.323 (s, 3 H, OMe), 1.017 (s, 3 H, C19), 0.974 (d, J = 5.9 Hz, 3 H, C21), 0.721 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 400 (M^+, $C_{27}H_{44}O_2$, 8), 385 (7), 368 (10), 345 (12), 111 (35), 105 (24), 91 (22), 71 (100), 55 (23).

THF adduct B (75b-M): R_f = 0.26 (hexanes/ether, 9:1); ^1H NMR (400 MHz) δ ($CDCl_3$) 3.866 (m, 2 H, THF C4), 3.690 (q, J = 7.4 Hz, 1 H, THF C2), 3.315 (s, 3 H, OMe), 1.012 (s, 3 H, C19), 0.969 (d, J = 6.6 Hz, 3 H, C21), 0.740 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 400 (M^+, $C_{27}H_{44}O_2$, 7), 385 (6), 368 (6), 345 (10), 111 (29), 105 (23), 91 (22), 71 (100), 55 (23).

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Electronic and Steric Control of α- versus β-Naphthyl Migratory Aptitudes in Enone Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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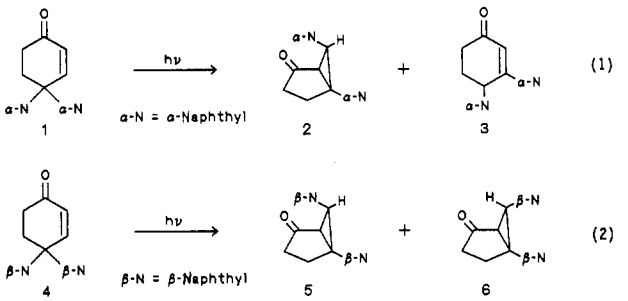
The photochemistry of 4-α-naphthyl-4-β-naphthylcyclohexenone was investigated. Photolysis afforded endo and exo isomers of 5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone and 5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone as well as 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone. The reaction was highly stereoselective with the 6-*endo*-naphthyl product being preferred both in the 6-α-naphthyl and the 6-β-naphthyl cases. Quantum yields were determined for the direct and sensitized reactions. In direct irradiations a ratio of 48:52 was observed for α- to β-naphthyl migration products while in sensitized photolyses the ratio was 41:59. Despite the differences between direct and sensitized runs, quenching studies revealed that the reacting species were triplets throughout. Excited-state triplet decay and reaction rates were determined. Interestingly, evidence was adduced for differential local excitation of α- and β-naphthyl moieties depending on the mode of energy transfer. A stereoselective triplet transfer from enone triplet to axial naphthyl in the direct irradiations and a statistical triplet excitation of axial and equatorial naphthyl groups in sensitization accounts for the results. Conformational information bearing on the photochemistry was obtained from molecular mechanics calculations.

Introduction

Since our discovery two and a half decades ago of the rearrangement of 4-arylcyclohexenones,[3] we have endeavored to expand the scope of the reaction and our understanding of its mechanistic details. Most recently, we reported[3g] the rearrangements of the 4,4-di-α-naphthyl- and 4,4-di-β-naphthylcyclohexenones (**1** and **4**, respectively) as in eq 1 and 2. The rearrangement of the α-naphthyl enone **1** was observed to proceed with ca. twice the efficiency and three times the triplet rate of the β-naphthyl enone **4**.



It was of considerable interest to compare α-naphthyl and β-naphthyl migratory aptitudes intramolecularly. Hence we proceeded to investigate the photochemistry of 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**7**).

Results

Synthesis of Photochemical Reactant and Two Potential Photoproducts. The synthesis of the dinaphthyl enone **7** is outlined in Scheme I. Also included in the scheme is the preparation of two potential photoproducts, 3-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**14**) and 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (**15**). A few points require comment. First, although the cis oxirane **8** is depicted, the corresponding trans isomer rearranged with equal facility and yield to afford aldehyde **9**. Also, the synthesis of the 3,4-enones **14** and **15** differed

(1) This is Paper 156 of our photochemical series and Paper 215 of the general series.

(2) (a) For Paper 213, see: Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 995-1007. (b) For Paper 214, see: Zimmerman, H. E.; Oaks, F. L.; Campos, P. *J. Am. Chem. Soc.* **1988**, *110*, 1007-1018.

(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. (c) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033-2047. (d) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879-886. (e) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887-896. (f) Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724-7732. (g) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732-7744. (h) Also, note that 4-arylcyclopentenones undergo a related rearrangement.[4]

(4) (a) Zimmerman, H. E.; Little, R. D. *J. Chem. Soc., Chem. Commun.* **1972**, 698-700. (b) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623-4630. (c) Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1972**, 226-227.

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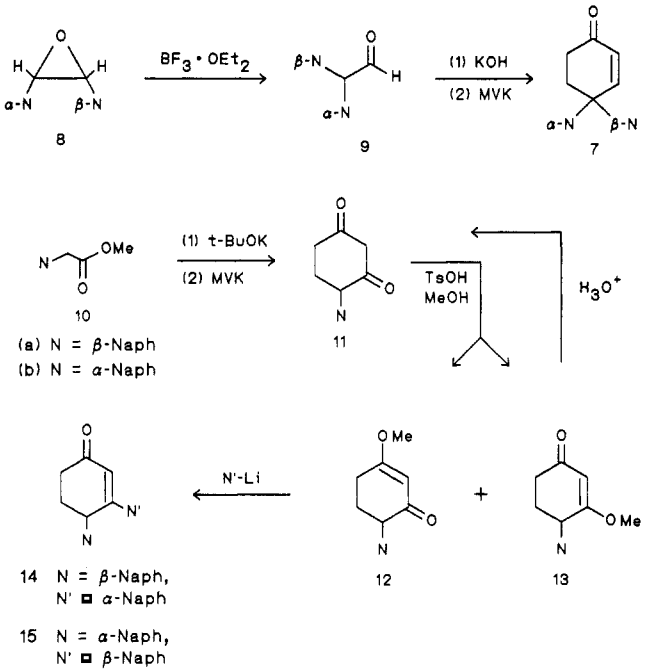
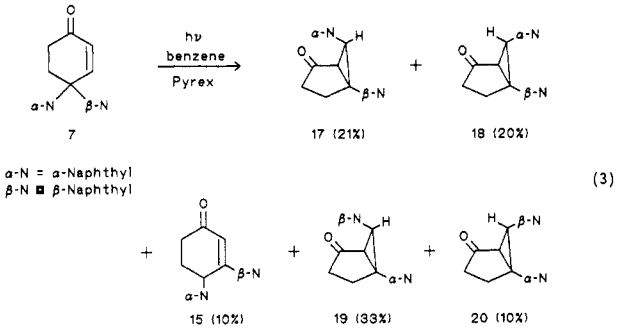
Scheme I. Synthesis of Dinaphthyl Enone 7 and Two Potential Photoproducts



from that in our original synthesis of 3,4-diphenyl-2-cyclohexenone (**16**), which utilized[3b] a Robinson condensation of methyl vinyl ketone and diphenylacetaldehyde. The approach in Scheme I proved more useful and also exploited the facile acid hydrolysis of enone ether **13**; recycling thus permitted higher conversions to the required enone ether **12**. Finally, the synthesis required differentiation of the two enol ether products **12** and **13**. This was accomplished by use of the Eu(fod)$_3$ shift reagent.[5a] A plot of the downfield shift of the naphthyl-substituted methine NMR absorption versus Eu(fod)$_3$ concentration is given in Figure 1 for each isomer,[5b] with the isomer exhibiting the greater shift being assigned structure **12**.

Exploratory Photochemistry of 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7). Photolysis of the dinaphthyl enone **7** to complete conversion in benzene led to five photoproducts as shown in eq 3. The NMR and



(3)

infrared spectral data of four of these suggested that they were 5,6-disubstituted bicyclo[3.1.0]-2-hexanones. The characteristic AB quartets also led to assignment of stereochemistry. For bicyclic ketones of this type one may generalize and assign cis and trans stereochemistry based on the coupling constants as outlined in Table I.

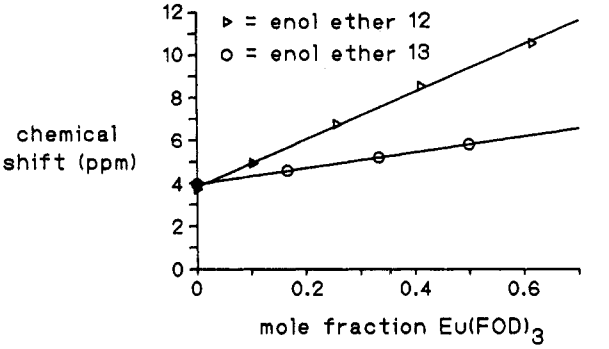


Figure 1. Plot of methine downfield NMR shifts versus Eu(fod)$_3$ concentration.

Table I. Cyclopropyl Coupling Constants in Bicyclo[3.1.0]-2-hexanones

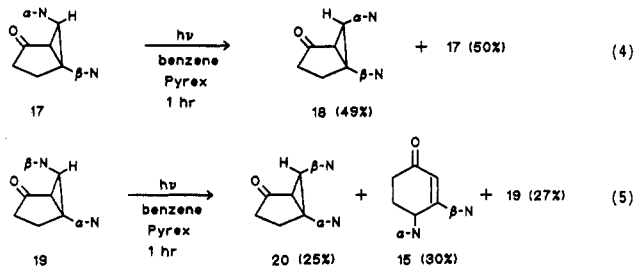
substitution	$J_{1,6}$, Hz cis	$J_{1,6}$, Hz trans	ref
5,6-diphenyl	4.5	9.6	3f
5-phenyl-6-*p*-anisyl	4.0	10.0	3c
5-phenyl-6-*p*-cyanophenyl	3.0	10.0	3c
5,6-dibiphenylyl	4.3	10.1	3f
5,6-di-α-naphthyl	a	9.6	3g
5,6-di-β-naphthyl	4.0	10.0	3g
5-α-naphthyl-6-β-naphthyl	3.2	9.6	*b*
5-β-naphthyl-6-α-naphthyl	3.7	9.3	*b*

[a] Cis isomer not available. [b] This publication.

Additionally, the fifth photoproduct was clearly an α,β-unsaturated ketone as evidenced by its infrared absorption at 1665 cm^{-1} and an NMR spectrum (note the experimental section) characteristic of a 3,4-diarylcyclohexenone. This product proved to be identical with the synthetic 3,4-enone **15**.

Firm structure elucidation of the five photoproducts was obtained by X-ray analysis. This was necessary since an assignment of (α-naphthyl–β-naphthyl) regiochemistry was not derivable from spectral data. A summary of the X-ray results is given in the Experimental Section, and ORTEP drawings as well as complete details are included in the supplementary material.

One facet of 4,4-diarylcyclohexenone photochemistry has been marked stereoselectivity with a preference for the 6-endo bicyclic isomer. The present formation of appreciable amounts of the 6-exo photoproducts **18** and **20** as outlined in eq 3 seemed likely not to be anomalous but due to subsequent equilibration. Indeed, in control runs the 6-endo bicyclic stereoisomers **17** and **19** were converted photochemically in 1 h to the 6-exo isomers to the extent of ca. 1:1 in analogy with bicyclic systems we have previously studied.[6] In addition, 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (**15**) was formed in the irradiation of the endo bicyclic ketone **19** (note equations 4 and 5).



(4)

(5)

(5) (a) Springer, C. R.; Meek, D. W.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 1105–1110. (b) The assumption of coordination of europium to the carbonyl oxygen in these systems has precedent.[5c] (c) Hart, H.; Love, G. M. *Tetrahedron Lett.* **1971**, 625–628.

(6) (a) Zimmerman, H. E.; Hancock, K. G.; Licke, G. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911. (b) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966.

Table II. Direct and Sensitized Quantum Yields for Dinaphthyl Enone 7

product	quantum yield[a,b] direct[c]	aceto[d]	thiox[e]
α-naphthyl migrated			
endo-6-α-naphthyl bicyclic **17**	0.40	0.31	0.33
exo-6-α-naphthyl bicyclic **18**	0.019	0.034	0.032
β-naphthyl migrated			
endo-6-β-naphthyl bicyclic **19**	0.35	0.38	0.39
3,4-dinaphthyl enone **15**	0.060	0.070	0.062
exo-6-β-naphthyl bicyclic **20**	0.046	0.050	0.045
total	0.88	0.84	0.86
α-naphthyl total[f]	0.42	0.34	0.36
β-naphthyl total[g]	0.46	0.50	0.50

[a] In benzene. [b] Error ±10%. [c] No additive, λ = 313 nm. [d] Acetophenone sensitized, λ = 334 nm. [e] Thioxanthone sensitized, λ = 366 nm. [f] Sum of α-naphthyl migrated products. [g] Sum of β-naphthyl migrated products.

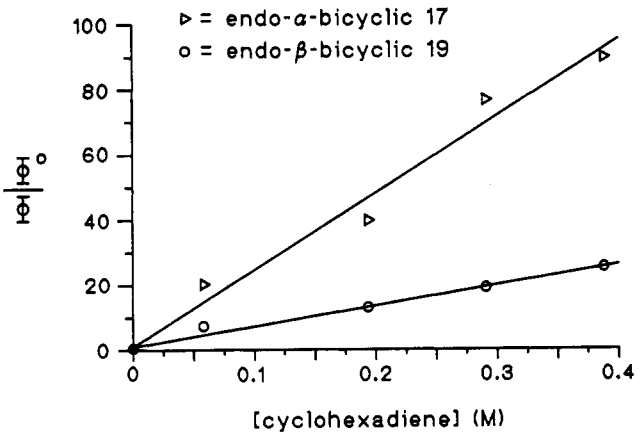


Figure 2. Stern–Volmer quenching plots for photoproducts **17** and **19**.

Finally, xanthone-sensitized irradiation of the dinaphthyl enone **7** afforded the same products in a distribution which was quite similar to that obtained on direct photolysis.

Low Conversion Regioselectivity and Quantum Yield Determinations. An item of primary concern was the relative extent of α-naphthyl versus β-naphthyl migration products. As noted in the Introduction, our previous work[3g] provided evidence for a greater migratory aptitude for the α-naphthyl group. For an intramolecular comparison, low conversion runs were needed to avoid complications due to the secondary photochemistry depicted in eq 4 and 5. Additionally, quantum yields were needed as a measure of the efficiencies of the rearrangements. The resulting quantum yields measured under direct and sensitized conditions are summarized in Table II.

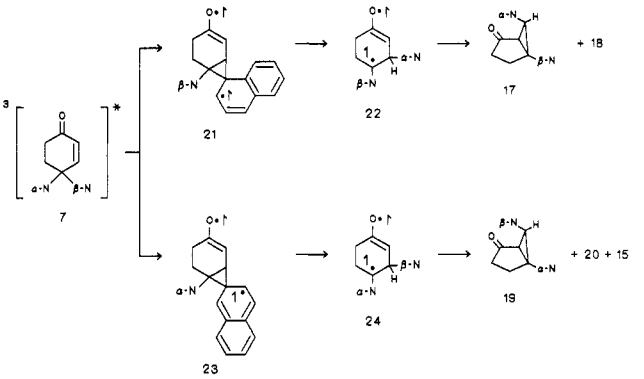
Interestingly, the product quantum yields showed the total of α-naphthyl to β-naphthyl migrated photoproducts in the direct irradiations to be in a 48:52 ratio and in sensitized runs to be 41:59. In direct irradiations, the product ratios were independent of whether the excitation wavelength was 313 nm, where the naphthyl groups absorb greater than 95% of the light, or 366 nm, where only the enone moiety absorbs (see Experimental Section). Also, it should be noted that the endo bicyclic stereoisomers predominated as anticipated. However, several aspects were unusual. In particular we note the lack of greater α-naphthyl over β-naphthyl migratory selectivity and the different product ratios obtained in direct versus sensitized photolyses. These points are considered below in the Discussion section.

Table III. Excited-State Lifetimes and Total Rates of Decay[a] for Enone 7

resulting product	slope[b]	τ, ns	$k_{d(tot)} \times 10^{-7}$, s^{-1}
endo-6-α-naphthyl bicyclic **17**	235.7	39.3 (78.6)	2.54 (1.3)
endo-6-β-naphthyl bicyclic **19**	62.5	10.4 (20.8)	9.60 (4.8)

[a] Lifetimes and rates have been calculated by using both 6×10^9 $L \cdot M^{-1} \cdot s^{-1}$ (ref 7a) and 3×10^9 $L \cdot M^{-1} \cdot s^{-1}$ (in parentheses, ref 7d) for the rate of quenching by cyclohexadiene in benzene. [b] Slope of Stern–Volmer plot from Figure 2.

Scheme II. Rearrangement Mechanism of the 4,4-Dinaphthyl Enone 7



Measurement of Excited-State Triplet Lifetimes and Decay Rates. With use of cyclohexadiene as a quencher, Stern–Volmer plots were obtained for the major photoproducts (i.e., *endo*-6-α-naphthyl bicyclic ketone **17** and *endo*-6-β-naphthyl bicyclic ketone **19**); these are shown in Figure 2. Excessive scatter precluded similar plots for the minor photoproducts (exo bicyclic products **18** and **20** as well as 3,4-enone **15**).

With the slopes being $k_q\tau$ and taking the rate of exothermic quenching (k_q) in benzene[7] as 6×10^9 $L \cdot M^{-1} \cdot s^{-1}$, we derived the lifetimes and their inverses (i.e., the $k_{d(tot)}$'s) listed in Table III. Interestingly, the plot for the α-naphthyl bicyclic photoproduct **17** had a slope that was close to 4-fold that of the plot for the β-naphthyl bicyclic photoproduct **19**. This suggests the presence of two noninterconverting triplets, each with its own lifetime and each one responsible for formation of one of the two types of photoproducts, α- or β-naphthyl migrated.

Normally at this point in triplet rate determinations, one would proceed to obtain excited-state rate constants. However, with a set of nonequilibrating excited states, the usual assumption that $k_r = \phi/\tau$ is too simplistic, and the matter of rate constants is delayed for the Discussion section.

Fluorescence and Phosphorescence Emission. An interesting and useful observation was that under conditions in which naphthalene and simple naphthalene derivatives emit intensely[8] (e.g., $\phi_f = 0.23$ for naphthalene[8b]), no fluorescence could be detected for the dinaphthyl enone **7**.

(7) (a) A rate of 6×10^9 $L \cdot M^{-1} \cdot s^{-1}$ has been measured for diene and oxygen quenching of triplet *p*-methoxyacetophenone in benzene.[7b] A similar rate has been observed for the quenching of several triplet species by stilbene.[7c] (b) Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539–1542. (c) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777. (d) Recent measurements based on a viscosity dependence afforded k_q as 3×10^9 $L \cdot M^{-1} \cdot s^{-1}$ for cyclohexadiene quenching of 4,4-diphenyl-2-cyclohexenone in benzene.[2a]

(8) (a) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1965.

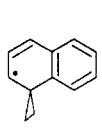
Phosphorescence emission was observed in methylcyclohexane–isopentane glass at 77 K, however, and was found to closely resemble that of naphthalene. The 0–0 emission peak was detectable as a shoulder, which corresponded closely in wavelength to the position of the 0–0 wavelength in the naphthalene spectrum. The triplet energy of enone **7** was thus determined as 60 kcal/mol.

Discussion

Reaction Course and Structural Aspects of the Mechanism. The first point we note is that the rearrangement of 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**7**) proceeds to form bicyclo[3.1.0]-2-hexanone products along with some 3,4-dinaphthylcyclohexenone. This profound rearrangement of cyclic enones to bicyclic ketones seems to be particularly general for enones having C-4 substituents with π-systems.[3,9]

Throughout, one mechanism can account for the reaction. This is applied in Scheme II to the 4,4-dinaphthyl reactant **7** of the present study. However, one may raise the question of whether the reaction is better categorized as an enone rearrangement or as a special case of the di-π-methane rearrangement[10] since the reaction involves the C=C π-bond of an enone moiety plus an aryl group bonded to C-4 of the cyclohexenone. In either case, the structural change is seen to be the same, with one of the naphthyl groups migrating via bridged intermediate **21** or **23** and subsequent closure or hydrogen migration by the resulting biradical **22** or **24** to the observed products.

Hitherto, both relative migration ability and absolute excited-state triplet rearrangement rate have been related to the ability of the migrating species to stabilize odd-electron density. Thus, in intramolecular migratory competitions *p*-cyanophenyl[3c,d] and anisyl[3c] were found to migrate 15 and 12 times as efficiently as phenyl, respectively. Further, the facility of aryl group migrations follows in the order α-naphthyl[3g] > β-naphthyl[3g] ≃ biphenylyl[3f] > phenyl[3b] in intermolecular comparisons of both efficiencies and rates. In the case of the α- versus β-naphthyl comparison, this makes theoretical sense on the basis of a bridged structure of the type **25** being more delocalized than a structure of the type **26**. This comparison derives either from counting resonance structures or from simple Hückel MO calculations.



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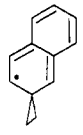

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Therefore it was quite surprising in the present study when an intramolecular competition between α-naphthyl and β-naphthyl groups led to a ratio of 48:52, slightly in favor of β-naphthyl migration. This apparent anomaly most likely arises from conformational effects or from excitation localization effects; this matter is discussed below.

Reaction Multiplicity and Efficiency. Having a basic mechanism in hand, we need to consider the reaction's multiplicity as well as one unique related feature, namely, its very high efficiency. It is quite clear that the rearrangement proceeds via the triplet excited state from the sensitization and the quenching experiments.

Thus, sensitization with xanthone, acetophenone, or thioxanthone led to the same products as observed in the direct irradiations. Quantitative differences were observed, however, and are considered below. Such sensitization data merely tell us that the triplet is capable of the observed rearrangement, not whether it is solely responsible for all of the reactivity. Additionally, the quenching of all reaction products by cyclohexadiene over a broad quencher concentration range provides further evidence for the presence of a triplet reactant. That only the triplet is involved derives from the fact that the Stern–Volmer quenching slopes are linear over a large concentration range of triplet quencher and do not flatten out at high concentrations.

The high rearrangement efficiency for dinaphthyl enone **7** (note Table V) is remarkable for simple cyclohexenones but not unusual for naphthyl- and biphenylyl-substituted cyclohexenones. One might be tempted to categorize these rearrangements into two groups: (i) those in which excitation is localized in the enone moiety and that are n–π* cyclohexenone rearrangements and (ii) those in which excitation is localized in a 4-aryl group and that are better viewed as di-π-methane rearrangements.[10] It is certainly true that in, for example, 4,4-diphenylcyclohexenone (**27**) the triplet excitation energy of a phenyl group is ca. 84 kcal/mol,[11] while the triplet energy of the enone moiety is 69 kcal/mol.[12] This means that in T_1, excitation is heavily localized in the enone chromophore. Conversely, in the naphthyl enones, the 61 kcal/mol energy[3g,13] of the naphthyl moiety leads to the prediction that T_1 will have the naphthyl group excited.

While the rearrangements of the two classes of enones are structurally the same, we note low quantum efficiencies for those having the enone excited and high quantum yields for those having the aryl moiety excited. One interpretation is that this effect derives from the longer lifetimes of the π–π* excited triplets of the aryl groups compared with the short lifetime of the enone moiety. In the case of naphthalene the triplet lifetime has been obtained[14] as 1 ms, while the lifetime of 4,4-dimethylcyclohexenone is ca. 30 ns.[15] Since quantum yields are given by the product of the rate of triplet rearrangement and the reactant triplet lifetime, even with equal rates of reaction, the enones having concentration of excitation in the aryl groups should have the greater reaction efficiencies.

(9) (a) Swenton, J. S.; Blankenship, R. M.; Sanitra, R. *J. Am. Chem. Soc.* **1975**, *97*, 4941–4947. (b) Nobs, F.; Burger, U.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 1607–1628.

(10) (a) A very early example of the di-π-methane rearrangement was the barrelene to semibullvalene rearrangement[10b] for which an interesting but incorrect mechanism was first suggested. The correct mechanism and the reaction generality was recognized in subsequent publications by the same group.[10c-g] (b) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183–184. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (d) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4191–4193. (e) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727. (f) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (g) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1983; Vol. 3.

(11) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905–913.

(12) (a) Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 6589–6595. (b) Zimmerman (Zimmerman, G. A. Ph.D. Thesis, University of Wisconsin, 1965) reported the 0–0 band of 4,4-diphenylcyclohex-2-enone at 416 nm.

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Table IV. Limits on Triplet Excitation Partitioning and Reaction Rates[a]

quantity[b]	lower limit	upper limit
F_A	0.42	0.54
F_B	0.46	0.58
k_{rA}	2.0×10^{-7}	2.5×10^{-7}
k_{rB}	7.6×10^{-7}	9.6×10^{-7}

[a] A refers to the state giving α-naphthyl migration and B the state undergoing β-naphthyl migration. [b] F_A and F_B are the fractions of light reaching states A and B, which rearrange with rates k_{rA} and k_{rB}, respectively.

Triplet Rates of Reaction. Evidence for Two Reacting States. As noted in the Results section, the Stern–Volmer $k_q\tau$ slopes of Figure 2 are different for formation of the α-naphthyl bicyclic photoproduct **17** and the β-naphthyl bicyclic photoproduct **19**. This requires different $k_q\tau$ values for the excited-state triplets leading to α-naphthyl and β-naphthyl migration products. We conclude that two noninterconverting triplets are present, each with its own $k_q\tau$ value. One attractive possibility is that one triplet (A) has the α-naphthyl group excited and the other (B) has the β-naphthyl group excited. Were triplet states A and B capable of equilibration on the time scale of the rearrangement and decay, a single, averaged Stern–Volmer slope would have been observed for all photoproducts.

Before identifying these triplets, we first obtain their rates of reaction (i.e. the k_r's) as in eq 6, derived from the

$$k_{rA} = \phi_A/(F_A\tau_A) \quad (6a)$$

$$k_{rB} = \phi_B/(F_B\tau_B) \quad (6b)$$

quantum yield expressions for photoproduct formation. In these, F_A and F_B are the fractions of the incident light utilized in producing excited states A and B. We note that all of the values needed to calculate the k_r's are known except for F_A and F_B. Further, it is possible to assign limits on F_A and F_B with the information at hand, as demonstrated in the Appendix. These limits are given by eq 7a and 7b.

$$\phi_A \le F_A \le (1 - \phi_B) \quad (7a)$$

$$\phi_B \le F_B \le (1 - \phi_A) \quad (7b)$$

Using the known quantum yields, we obtain the limits on F_A and F_B. Now, with these available, we can utilize eq 6a and 6b to obtain limits on the rates of the two triplet excited states rearranging. These results are given in Table IV. We note that the ranges of these limits are small.[16]

We still have not established the nature of excited states A and B. In the discussion below, A is taken as the excited state responsible for α-naphthyl migration and B is the excited state undergoing β-naphthyl migration.

Excited-State Processes Occurring in Direct Irradiation. As noted in the Results section, independent of whether light was primarily absorbed by the enone moiety (i.e., at 366 nm) or by the naphthyl groups (i.e., at 313 nm), the same product distribution was observed as well as the same reaction efficiency. That the reaction is a triplet process is established by the quenching studies. Hence, singlet excitation initially localized in either a naphthyl or the enone moiety results in the formation of the same distribution of triplets A and B. This suggests a common pathway in triplet generation from either starting singlet; that pathway most likely is intersystem crossing in the locus of the enone carbonyl group. We do know that spin–orbit coupling results in exceptionally facile and rapid intersystem crossing at the carbonyl oxygen,[17] while intersystem crossing in naphthyl compounds tends to be slow.[18] Furthermore, absorption of light by a naphthyl moiety and singlet energy transfer to the enone group is exothermic (90 kcal/mol[19] → 76 kcal/mol[12]), and rapid exothermic singlet energy transfer is known to occur over long distances.[20] This view is supported by the absence of naphthyl fluorescence in dinaphthyl enone **7**.

Thus, independent of which chromophore absorbs light, one anticipates triplet excitation to be engendered at the carbonyl group.[2a] This triplet excitation is now capable of transfer to the naphthyl chromophores. Not only is triplet energy transfer from the enone carbonyl to the naphthyl groups exothermic (69 kcal/mol[21] → 61 kcal/mol[13]) but literature precedent[2a] suggests competitive triplet transfer from a triplet cyclohexenone moiety to a ground-state naphthyl group when these are separated by one methylene group and a saturated ring carbon. In this instance, the naphthyl and enone moieties are less separated and overlap between the β-enone carbon and a naphthyl group is possible.

Finally, evidence is presented below, in connection with sensitization and quenching observations, that the two reacting triplets (A and B) have excitation localized in the naphthyl groups.

Reactivity Observed in Sensitization Contrasted with the Direct Photochemistry. As in the direct irradiations, upon sensitization it is the naphthyl groups that are triplet excited. This follows from the observation (see Table II) of the same quantum efficiencies in both acetophenone (E_T 74 kcal/mol[22]) and thioxanthone (65 kcal/mol[13a]) sensitization. With the known triplet energies of the naphthyl moiety (61 kcal/mol[13]) and the enone chromophore (69 kcal/mol[21]), rapid exothermic transfer from thioxanthone can only occur to the naphthyl groups. Because the same efficiencies are observed with both sensitizers, we conclude that intermolecular delivery of triplet excitation is selective to the naphthyl groups.

(16) The limits in Table IV are remarkably tight. This arises as a consequence of the high total quantum yields. Thus, ϕ_A and $(1 - \phi_B)$ are necessarily close when the sum of these efficiencies is close to unity. Hence the method is of particular use for high efficiency processes.

(17) (a) A rate of S_1–T_1 intersystem crossing of 2×10^{11} s^{-1} has been reported for benzophenone,[17b-d] while a rate of 10^{12} s^{-1} has been measured for acetophenone.[17e] (b) Rentzepis, P. M. *Science* **1970**, *169*, 239–247. (c) Rentzepis, P. M.; Busch, G. E. *Mol. Photochem.* **1972**, *4*, 353–367. (d) Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500–2511. (e) Hirata, Y.; Lim, E. C. *Chem. Phys. Lett.* **1980**, 167–170.

(18) (a) Rates of intersystem crossing have been measured as 10^6 s^{-1} for naphthalene[18b] and 5×10^7 s^{-1} for 1-methylnaphthalene.[18c] (b) Kasha, M. *Disc. Faraday Soc.* **1950**, *9*, 14–19. (c) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.

(19) (a) The singlet energy for naphthalene has been reported as 92 kcal/mol and that for 1-methylnaphthalene as 90 kcal/mol.[19b] (b) Reference 18c, p 70.

(20) (a) Singlet–singlet energy transfer from naphthyl to benzoyl moieties over 7 Å has been found to occur with a rate ca. 10^9 s^{-1} by a through-bond exchange mechanism[8a,20b] paralleling the Dexter triplet–triplet exchange mechanism.[20c] Rapid singlet transfer may also occur over separations of up to 100 Å[20d] by a dipole coupling mechanism.[20e] (b) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645. (c) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850. (d) Stryer, L.; Haugland, R. P. *Proc. Natl. Acad. Sci.* **1967**, *58*, 720–726. (e) Förster, T. *Disc. Faraday Soc.* **1959**, *27*, 7–17.

(21) (a) The vertical spectroscopic triplet energy of 4,4-diphenylcyclohexenone has been reported as 69 kcal/mol.[12b] Recently, a 61–63 kcal/mol cyclohexenone transient absorbing at 280 nm has been observed,[21b,c] which has been suggested to be a twisted (π–π^*) triplet[15a] or ground-state[15b] enone species. (b) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816–3822. (c) Pienta, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2704–2705.

(22) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468.

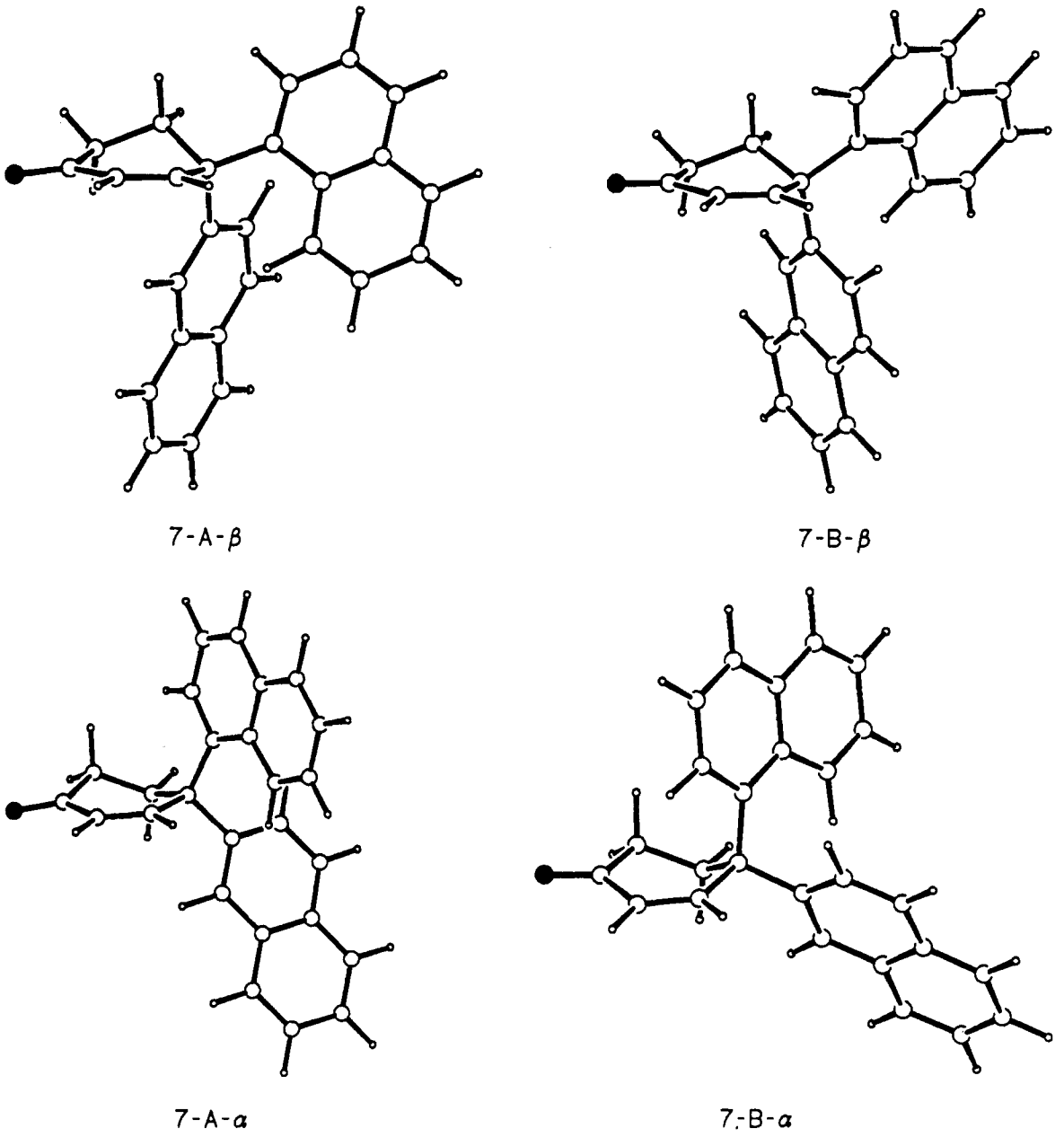


Figure 3. Four lowest energy conformations of enone 7 (● represents oxygen).

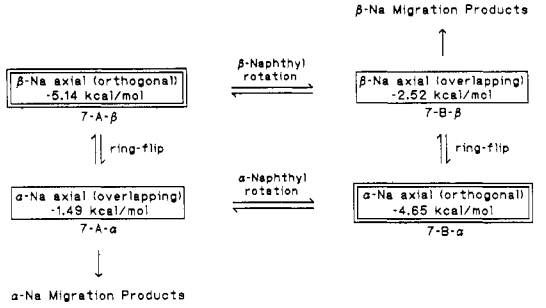
Interestingly, while the same reactions occur on acetophenone and thioxanthone sensitization as in the direct irradiations, the product ratios differ appreciably beyond experimental error[23] (Table II). The major effect is seen in the efficiency of formation of the endo α-naphthyl bicyclic ketone **17**, which is lower on sensitization than in direct irradiations. Also, the efficiency of β-naphthyl migration to products **19**, **20**, and **15** is seen to rise slightly upon sensitization.

Hence, the relative ease of α-naphthyl migration and β-naphthyl migration depends on whether the group is excited via intramolecular triplet energy transfer or, instead, by delivery of energy from an external triplet donor. An understanding of this difference requires consideration of the conformations available to the reactant and its excited state. Both the ground-state enone and its excited states are in pseudochair conformations, and a large number of conformations are a priori possible. Much of this derives from there being six rotamers possible for each naphthyl group present, α or β. Fortunately, the situation is simplified, since only four conformers are of interest in the context of the observed reactivity.

Four points need to be made. One is that for axial groups, just those rotational conformers in which the π-system is aimed toward the β-carbon of the enone moiety should be reactive. Second, for a given axial naphthyl group the reactive conformer is only the second lowest in energy (see Scheme III). Third, the lowest energy conformations are predicted to be unreactive because the axial naphthyl and enone π-systems are oriented orthogonal to one another. Fourth, when the equatorial group in these lowest energy conformations becomes axial through a ring-flip of the cyclohexenone, the resulting rotational orientation of its π-system is toward the enone π-system (i.e., reactive). The interrelationships of these conformers are given in Scheme III, and the conformers themselves are depicted in three dimensions in Figure 3.

(23) It needs to be noted that although our quantum yields are generally given with ±10% error limits, our reproducibility is generally given as ±5%. Hence, the differing direct and sensitized ratios and efficiencies are real. As has been noted by one referee, the precision in the present paper is generally better. However, since experimental difficulties differ from system to system, it seems better to be conservative and give a limit applicable to all of our studies.

Scheme III. Interrelationship of the Major Conformations of Dinaphthyl Enone 7



The lowest energy conformers are **7-A-β** and **7-B-α**. Here "A" refers to conformers leading onward to α-migration products and "B" refers to conformers affording β-migration. The "α" versus "β" designation indicates which naphthyl group is axial in that conformer. These lowest energy conformers have the axial naphthyl π-system orthogonal to the enone π-system.

Each of the next two lowest energy conformations, **7-A-α** and **7-B-β**, also have a naphthyl group axial, but now with its π-system overlapping nicely with the enone moiety. The relative energies of the four conformations, as obtained from MMP2,[24] are included in Scheme III. One interesting point is that the "A" conformers are interconverted by a pseudochair–pseudochair enone ring inversion which should be facile.[25] The same is true of the "B" conformers. Conversely, the "α" and "β" conformers are interconverted only by synchronous rotation of the bulky naphthyl groups, which molecular mechanics indicates should be difficult (ca. 13 kcal/mol for α-naphthyl axial and 7 kcal/mol for β-naphthyl axial; see Experimental Section). Hence, in the absence of naphthyl rotations, excitation of the "A" series conformers can lead only to α-naphthyl migration, while excitation of "B" series conformers affords only β-naphthyl migration products.

We now address the relevance of these stereochemical considerations to the photochemical reaction. First, consider the mechanism occurring in direct irradiation. It has been noted above that the facile intersystem crossing in the vicinity of a carbonyl group results in triplet excitation being "born" in the enone moiety. Although conformers **7-A-α** and **7-B-β** are formed only in small amounts due to their higher steric energies, they possess favorable 1,3-conjugation between their axial naphthyl group and the enone β-carbon. This interaction should lead to selective excitation of the axial naphthyl group in these conformations by intramolecular transfer from the enone moiety. Further, these conformers are capable of reaction due to the enhanced naphthyl–enone overlap. In view of there being ca. a 1:1 distribution of "A" versus "B" molecules, the observation (note Table II) of nearly equal efficiencies for α-naphthyl versus β-naphthyl migration is understood. Direct excitation of an "A" conformer will lead ultimately to α-naphthyl migration, while excited "B" conformers will afford only β-naphthyl migration. This discussion does assume that the natural enone triplet lifetime is sufficient to permit population by ring-flip of the **7-A-α** and **7-B-β** conformer triplets prior to decay. This is required in view of the high (i.e., $\phi = 0.88$) total reaction efficiency.

Another point deals with the observed α-naphthyl versus β-naphthyl migration rates. If we think of population of the reactive **7-A-α** and **7-B-β** conformers as a preequilibrium process followed by a rate-limiting naphthyl migration, we recognize that the less favorable ring-flip bringing the bulky α-naphthyl group axial to afford **7-A-α** will lead to an inhibited overall experimental rate of rearrangement (i.e., k_{rA}). Again, we assume that despite the unfavorable preequilibrium, the excited-state lifetime is sufficient to assure that most "A" triplets will undergo α-naphthyl migration prior to decay or rotation to give "B" triplets.

In sensitization there is reason[2a] to believe that the probability of collision of the sensitizer molecule with each of the different naphthyl groups controls which of the two alternative naphthyls in each molecule receives the triplet excitation. Differences in steric hindrance to such collisions are not apparent from inspection of models, and we may assume this energy transfer to be nearly statistical to both α-naphthyl and β-naphthyl groups in both pseudoaxial and pseudoequatorial positions.

Let us first consider sensitization of pseudoequatorial groups in the lowest energy conformations. In each case, conformational equilibration by cyclohexenone ring-flip leads to a reactive conformation. Thus, energy transfer to the equatorial α-naphthyl group of **7-A-β** leads onward to conformer **7-A-α**, which rearranges by α-naphthyl migration. Similarly, energy transfer to the equatorial β-naphthyl group of **7-B-α** leads to conformer **7-B-β**, which rearranges by β-naphthyl migration. We might conclude at this point that the situation is precisely that observed in direct irradiation, except that if only equatorial groups in the low energy conformations were ultimately reactive, one would observe exactly half of the quantum yields seen in direct irradiation. The sensitization of unreactive axial naphthyl groups in the lowest energy conformers accounts for the 50% loss.

Because the sensitized quantum yields are not lowered by 50%, we do need to consider the consequence of the triplet sensitization of axial naphthyl groups in the lowest energy conformations. As suggested above, these lowest energy conformations have virtual orthogonality between the naphthyl and enone chromophores, and in each case a cyclohexenone ring-flip merely affords an equatorial excited naphthyl species also incapable of reaction. Thus, in order to react, the less favorable conformational change of naphthyl rotation must occur to interconvert the "A" and "B" series conformers. In this way **7-A-β** with its excited axial β-naphthyl group leads to **7-B-β**, which affords β-naphthyl migration products. This particular rotation seems to be accessible. However, excitation of the axial α-naphthyl group of **7-B-α** requires a rotation of the axial α-naphthyl group to give **7-A-α**, a particularly difficult rotational process. Since this route leads onward to α-naphthyl migration, we would anticipate a diminution of α-naphthyl migration product upon sensitization as observed.

Having presented one rationale for the enhanced β-naphthyl migratory aptitude in direct irradiation compared with simple electronic expectation, we observe that a minor variation on this picture is precisely parallel in nature and prediction. Inspection of models and of Figure 3 reveals that the pseudoequatorial naphthyl groups in the lowest energy conformations **7-A-β** and **7-B-α** have their π-systems overlapping to some extent with the enone π-system, although this overlap is less ideal than in the reactive pseudoaxial naphthyls of the higher energy conformers **7-A-α** and **7-B-β**. Thus, in direct irradiation these equa-

(24) Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399–403.

(25) (a) Although a barrier to ring inversion of 10.4 kcal/mol has been measured for 2-cyclohexenone,[25b] a better model for the triplet excited enone would be the radical anion of 2-cyclohexenone which has a barrier of ca. 5 kcal/mol.[25c] (b) Wieser, H.; Smithson, T. L.; Kruger, P. J. *J. Mol. Spectrosc.* **1982**, *99*, 368–377. (c) Elson, I. H.; Kemp, T. J.; Stone, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 7091–7093.

Table V. Summary of Reaction Efficiencies and Triplet Excited-State Rates[a] of Rearrangement and Decay for 4,4-Diaryl-2-cyclohexenones

substituents	ϕ_{tot}	$k_r \times 10^{-8}$, s^{-1}	$k_{d(tot)} \times 10^{-8}$, s^{-1}	ref
4,4-diphenyl	0.043	0.23 (0.11)	5.0 (2.5)	3b
4-(*p*-cyanophenyl)-4-phenyl	0.18	2.0 (1.0)	9.2 (4.6)	*b*
	0.016	1.9 (0.93)	9.2 (4.6)	*c*
4,4-dibiphenylyl	0.36	1.3 (0.65)	3.4 (1.7)	3f
4,4-di-α-naphthyl	1.00	1.7 (0.85)	1.7 (0.85)	3g
4,4-di-β-naphthyl	0.40	0.55 (0.28)	1.4 (0.70)	3g
4-α-naphthyl-4-β-naphthyl	0.84	0.21 (0.11)	0.25 (0.13)	*d, e*
	0.92	0.88 (0.44)	0.96 (0.48)	*d, f*

[a] Rates have been calculated by using both 6×10^9 $L \cdot M^{-1} \cdot s^{-1}$ (ref 7a) and 3×10^9 $L \cdot M^{-1} \cdot s^{-1}$ (in parentheses, ref 7d) for the rate of quenching by cyclohexadiene in benzene. [b] *p*-Cyanophenyl migrating (ref 3d). [c] Phenyl migrating (ref 3d). [d] Assuming 50% population of each state. [e] α-Naphthyl migrating (this study). [f] β-Naphthyl migrating (this study).

torial naphthyl groups can be excited by intramolecular energy transfer from the enone, and as noted in our fourth point above, an enone ring-flig brings these excited groups into the reactive conformation. However, again, the α-naphthyl groups are confronted by a larger energy barrier to becoming axial. This equatorial excitation process can be considered a distinct mechanism or may simply provide an additional channel leading to products.

The discussion above regarding sensitization applies equally well when this alternative direct irradiation mechanism is considered. However, with this second mechanism for reaction in direct irradiation, one might wonder whether triplet sensitization of an "unreactive" axial naphthyl group might not lead by ring-flip to an equatorially excited conformer, which has been said to be reactive by virtue of a ring-flip. It needs to be emphasized that the equatorially excited species thus formed is not related by ring-flip to a reactive axial conformers, but only back to its unreactive conformation.

Excitation Energy Leakage between Naphthyl Groups. One possibility not yet considered is intramolecular triplet excitation transfer between naphthyl groups.[26] It has been noted that this cannot be rapid compared with the rates of rearrangement since two distinct excited states were detected in quenching studies. However, some such leakage may occur, and in particular might provide a pathway for energy utilization when an orthogonal and unreactive pseudoaxial naphthyl group is excited by sensitization.

Further evidence bearing on this point is found in the behavior of 4,4-di-α-naphthylcyclohexenone in which unit efficiencies were observed[3g] both in direct and sensitized photolyses. With attention focussed on orthogonal pseudoaxial α-naphthyl groups excited in sensitization, it is recognized that this excitation cannot be dissipated in this case. It seems likely that in this system one has internaphthyl energy transfer affording the equatorial excited α-naphthyl group, which can react following a ring-flip.

Summary of 4,4-Diarylcyclohexenone Reactivities. Quantum yields and triplet rearrangement rates are compiled in Table V, which includes the quantum efficiencies and rates for the present study as well as related compounds for comparison. For the enones studied prior to the present investigation, reactivity seemed to be governed primarily by electronic effects. However, it is now clear that steric effects may play a dominant role, especially in the case of systems such as the present one, which possess very bulky substituents.

One interesting point regards the rearrangement of 4,4-di-α-naphthylcyclohexenone, in which extra relief of steric strain results upon migration of one of the two α-naphthyl groups. This would account for the rapid rate of triplet rearrangement and the high efficiency. It is likely that a similar strain relief effect is a contributory factor in the high efficiency observed in the present study as well.

Conclusion. One of the aims of organic photochemical research is the discovery of reactions that are particularly general. The number is still limited compared with ground-state organic chemistry. It does appear, however, that the rearrangement of 4-arylcyclohexenones to afford bicyclo[3.1.0]hexanones has become one of those general photochemical reactions.

Experimental Section[27]

α-Naphthyl-β-naphthylethanal (9). Employing a modification of the method of Reif and House,[28] to a solution of 5.00 g (0.0169 mol) of *cis*-1-α-naphthyl-2-β-naphthyloxirane[29] (8) in 150 mL of benzene was added 1.06 mL (1.20 g, 8.44 mmol) of freshly distilled boron trifluoride etherate. The mixture was allowed to react for 2 min, quenched with water, and washed with water until pH 6. Neutral workup gave 5.31 g of a yellow oil, which was chromatographed on a 3 × 50 cm silica gel column eluted with 2% ether in hexane, with 200-mL fractions being collected to give the following: fraction 5, 150 mg of a yellow solid not further characterized; 6–12, 4.80 g (95.8%) of the dinaphthylethanal as a yellow oil. The oil was insufficiently stable for elemental analysis.

The spectral data for α-naphthyl-β-naphthylethanal were the following: IR ($CDCl_3$) 3080, 2950, 2820, 2720, 1735 (C=O), 1600, 1500, 1406, 1320, 1280, 1175, 1130, 855, 820, 795, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.164 (d, J = 1.97 Hz, 1 H, C*H*O), 7.25–8.25 (m, 14 H, aryl), 5.781 (br s, 1 H, C*H*CHO); MS m/e 296.1201 (calcd for $C_{22}H_{16}O$, m/e 296.1201).

4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7). Adapting the method of Zimmerman, Caufield, and King,[3g] to a solution of 4.26 g (0.0144 mol) of α-naphthyl-β-naphthylethanal (9) in 125 mL of THF at 0 °C was added dropwise 1.60 mL (4.82 mmol) of 3 N potassium hydroxide in ethanol. To this amber solution was added 1.80 mL (1.55 g, 0.0222 mol) of methyl vinyl ketone over 30 min, and after warming to room temperature over 7 h, the mixture was refluxed for 68 h. The solution was poured into 80 mL of 10% hydrochloric acid, and basic workup with ether yielded 5.2 g of a maroon oil. Chromatography on a 4 × 60 cm silica gel column eluted with 5.13 L of 4% and 5.99 L of 10% ethyl acetate in hexane, with 45-mL fractions being collected gave the following: fractions 80–134, 1.49 g of a solid not further characterized; 135–245, 2.70 g of the dinaphthyl enone, mp 136–141 °C. The product was filtered through 1:1 silica gel–Norite eluted

(26) There are still further mechanistic schemes. One might consider that in sensitization, there is an unequal probability of collision of sensitizer with α- versus β-naphthyl groups with a slight preference for the latter. Another possibility is that there is some α- to β-naphthyl (i.e., axial to equatorial) energy transfer in the case of the unreactive axial conformers.

(27) All reactions were run under dry nitrogen with solvents purified as described previously.[3] Neutral workup refers to dilution with the indicated solvent, washing with water and brine, drying over magnesium sulfate, filtration, and concentration in vacuo. Basic workup included a washing with saturated aqueous sodium bicarbonate prior to the water wash. All melting points were determined with a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) or basic alumina (Fisher Scientific, 80–200 mesh) mixed with 1% (v/v) Sylvania green phosphor and slurry-packed into Vycor quartz columns, permitting monitoring with a hand-held ultraviolet lamp. Plates for preparative thick-layer chromatography (TLC) were prepared with MN-Kieselgel G/UV 254 silica gel. High performance liquid chromatography (HPLC) was performed on a system incorporating an LDC 5000 psi minipump and an LDC 254 nm detector. For analyytical HPLC, a 0.46 × 60 cm polished stainless steel column packed with 4–6-μm porous silica gel beads was employed. For preparative HPLC, a 0.95 × 50 cm steel column packed with 8–12-μm porous silica gel beads was used.

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

(29) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229–2235.

with 10% ethyl acetate in hexane and then recrystallized from ether in hexane to yield 2.13 g (45.8%) of white plates, mp 151–152 °C.

The spectral data for 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone were the following: IR (KBr) 3040, 2950, 2920, 2860, 1687 (C=O), 1600, 1515, 862, 827, 807, 787, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.05–7.95 (m, 15 H, aryl + C(O)CH=C*H*), 6.28 (d, J = 9.88 Hz, C(O)C*H*=CH), 3.16 (m, 1 H, C(O)C*H*HCH$_2$), 2.95 (m, 1 H, C(O)CH*H*CH$_2$), 2.42 (m, 2 H, C(O)CH$_2$C*H*$_2$); MS m/e 348.1490 (calcd for $C_{26}H_{20}O$, m/e 348.1514); UV (ethanol) λ_{max} (ε) 312 (910), 290 (8524), 280 (10780), 278 (10762), 271 (10624), 263 (9422).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.85; H, 5.87.

General Procedure for Exploratory Photolysis. All exploratory irradiations were performed in an immersion apparatus with a 450-W Hanovia medium-pressure mercury lamp equipped with a Pyrex filter (λ > 280 nm). All solutions were purged with deoxygenated and dried nitrogen[30] for 1 h prior to and during photolysis.

Exploratory Direct Photolysis of 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7). A solution of 160 mg (0.459 mmol) of 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (7) in 150 mL of benzene was photolyzed for 10 min. Concentration in vacuo yielded 161 mg of a yellow oil, which was chromatographed on a 2.5 × 70 cm silica gel column eluted with 4.4 L of 2.0% and 1.7 L of 3.0% ethyl acetate in hexane, with 45-mL fractions being collected to give the following: fractions 25–41, 53.0 mg (33.1%) of *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (**19**); 42–60, 33.5 mg (20.9%) of *trans*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (**17**); 61–80, 6.5 mg (4.1%) of recovered **7**; 117–150, 64.8 mg of a material shown by ^1H NMR to be a 2:1:1 mixture (20.2%, 10.1%, and 10.1%) of *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (**18**), *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (**20**), and 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (**15**), respectively.

The mixture of cis bicyclics and 3,4-dinaphthyl enone was applied to a 20 × 20 cm preparative TLC plate and eluted 20 times with 50% dichloromethane in pentane to give the following: band 1, R_f = 0.43, 50.5 mg of a 3:1 mixture of *cis*-6-α-naphthyl bicyclic **18** and *cis*-6-β-naphthyl bicyclic **20**, respectively; 2, R_f = 0.25, 11.5 mg (7.2%) of 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (**15**).

The mixture of cis bicyclics was subjected to preparative HPLC eluted with 50% dichloromethane in hexane to give the following: peak 1, R_f = 7.13 h, 12.3 mg (7.7%) of *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (**20**); 2, R_f = 7.5 h, 28.7 mg (17.9%) of *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (**18**).

The *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone was recrystallized from ether in hexane to yield 45.3 mg (28.3%) of white prisms, mp 159–160 °C. The *trans*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone was recrystallized from ether in hexane to afford 25.6 mg (16.0%) of white needles, mp 156–157 °C. The 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone was recrystallized from ether in hexane to give 9.7 mg (6.1%) of pale yellow prisms, mp 79–80 °C. The *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone was recrystallized from ether in hexane to yield 7.5 mg (4.5%) of white plates, mp 189–190 °C. The *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone was recrystallized from ether in hexane to afford 24.9 mg (15.6%) of white prisms, mp 132–133 °C.

The spectral data for *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone were the following: IR (KBr) 3035, 2940, 1730 (C=O), 1600, 1505, 1460, 1409, 1390, 1310, 1300, 1270, 1255, 1207, 1190, 1145, 1105, 925, 867, 820, 799, 778, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.72–8.15 (m, 7 H, aryl), 7.45–7.70 (m, 7 H, aryl), 3.456 (d, J = 9.58 Hz, 1 H, cyclopropyl), 2.782 (d, J = 9.58 Hz, 1 H, cyclopropyl), 2.50 (m, 3 H, C(O)CHHCC*H*$_2$ and *exo*-C(O)CH*H*CH$_2$), 2.28 (dd, J = 18.1, 9.0 Hz, *endo*-C(O)C*H*HCH$_2$); MS m/e 348.1510 (calcd for $C_{26}H_{20}O$, m/e 348.1514); UV (95% ethanol) λ_{max} (ε) 321 (415), 317 (1056), 306 sh (2675), 296 sh (11876), 287 (17829), 277 (16286), 266 sh (11026), 261 (9281), 256 (7949).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.87; H, 6.09.

The spectral data for *trans*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone were the following: IR (KBr) 3035, 2910, 1705 (C=O), 1625, 1590, 1500, 1450, 1401, 1380, 1318, 1300, 1260, 1195, 1178, 1081, 1020, 1002, 960, 940, 875, 849, 805, 777, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.11 (d, J = 7.43 Hz, 1 H, aryl), 7.90 (m, 6 H, aryl), 7.52 (m, 7 H, aryl), 3.368 (d, J = 9.34 Hz, 1 H, cyclopropyl), 3.088 (d, J = 9.34, 1 H, cyclopropyl), 2.550 (t, J = 9.44 Hz, 1 H, *endo*-C(O)CH$_2$C*H*H), 2.341 (dd, J = 9.44, 10.54 Hz, 1 H, *exo*-C(O)CH$_2$CH*H*), 2.185 (dd, J = 10.54, 19.05 Hz, 1 H, *exo*-C(O)CH*H*CH$_2$), 1.263 (dd, J = 9.44, 19.05 Hz, 1 H, *endo*-C(O)C*H*HCH$_2$); MS m/e 348.1513 (calcd for $C_{26}H_{20}O$, m/e 348.1514); UV (95% ethanol) λ_{max} (ε) 325 (380), 318 (1065), 306 sh (3610), 298 sh (9238), 288 (13853), 280 (13133), 272 sh (10542), 262 (8098).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.33; H, 5.91.

The spectral data for 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone were the following: IR ($CDCl_3$) 3090, 3015, 2970, 2950, 2880, 1665 (C=O), 1600, 1345, 1320, 1249, 1209, 1193, 850, 813, 799 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.28 (d, J = 7.43 Hz, 1 H, aryl), 7.91 (d, J = 7.43 Hz, 1 H, aryl), 7.89 (s, 1 H, aryl), 7.65 (m, 6 H, aryl), 7.36 (m, 5 H, aryl), 7.003 (s, 1 H, vinyl), 5.278 (dm, J = 5.02, <1 Hz, 1 H, methine), 2.65 (m, 1 H, CH$_2$CH$_2$), 2.39 (m, 3 H, CH$_2$CH$_2$); MS m/e 348.1507 (calcd for $C_{26}H_{20}O$, m/e 348.1515); UV (ethanol) λ_{max} (ε) 344 sh (3637), 312 (13384), 298 (12415), 274 (22102), 226 sh (18853), 222 (38817).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.59; H, 5.44.

The spectral data for *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone were the following: IR (KBr) 3041, 3000, 2916, 1717 (C=O), 1590, 1502, 1408, 1351, 1282, 1250, 1229, 1211, 1181, 1157, 1137, 1102, 1036, 1006, 905, 891, 880, 852, 840, 816, 792, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.10 (m, 0.67 H, aryl), 7.90 (d, J = 7.75 Hz, 0.33 H, aryl), 7.23–7.77 (m, 11.34 H, aryl), 7.03 (t, J = 7.74, 0.33 H, aryl), 6.88 (d, J = 7.45, 0.33 H, aryl), 6.78 (dd, J = 8.64, 2.08 Hz, 0.67 H, aryl), 6.49 (dd, J = 8.64, 1.63 Hz, 0.33 H, aryl), 3.246 (d, J = 3.19 Hz, 0.67 H, cyclopropyl), 3.060 (d, J = 3.19 Hz, 0.33 H, cyclopropyl), 2.98 (m, 1 H, *exo*-C(O)CH$_2$C*H*), 2.904 (d, J = 3.19 Hz, 0.33 H, cyclopropyl), 2.871 (d, J = 3.19 Hz, 0.67 H, cyclopropyl), 2.47 (m, 3 H, C(O)C*H*$_2$CH$_2$ and *endo*-C(O)CH$_2$C*H*H); MS m/e 348.1514 (calcd for $C_{26}H_{20}O$, m/e 348.1515); UV (ethanol) λ_{max} (ε) 312 sh (1093), 296 sh (7477), 284 (11158), 273 (10675), 222 (57737).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.60; H, 5.75.

The spectral data for *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone were the following: IR ($CHCl_3$) 3020, 3005, 2980, 1723 (C=O), 1596, 1508, 1235, 1172, 1021, 966, 950, 930, 911, 858, 818, 795 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.19 (d, J = 9.45 Hz, 1 H, aryl), 7.72 (d, J = 10.12 Hz, 1 H, aryl), 7.05–7.66 (m, 12 H, aryl), 3.389 (d, J = 3.69 Hz, 1 H, cyclopropyl), 3.192 (d, J = 3.69 Hz, 1 H, cyclopropyl), 3.10 (m, 1 H, *exo*-C(O)CH$_2$CH*H*), 2.64 (m, 3 H, C(O)C*H*$_2$CH$_2$ and *endo*-C(O)CH$_2$C*H*H); MS m/e 348.1514 (calcd for $C_{26}H_{20}O$, m/e 348.1514); UV (95% ethanol) λ_{max} (ε) 326 (281), 317 (853), 310 sh (1607), 298 sh (7536), 287 (11233), 278 (10 9632), 261 sh (8374), 256 sh (9044).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.40; H, 5.83.

Exploratory Xanthone-Sensitized Photolysis of 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7). A solution of 503 mg (1.44 mmol) of 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**7**) and 10.0 g (51.0 mmol) of xanthone in 500 mL of benzene was photolyzed for 25 min. Concentration in vacuo gave 15.3 g of a yellow oil, which was chromatographed on a 2 × 90 cm silica gel column eluted with 5.42 L of 1.0%, 12.02 L of 1.5%, and 0.59 L of 5.0% ethyl acetate in hexane, with 45-mL fractions being collected to give the following: fractions 46–85, 9.8 g of xanthone; 86–121, 167 mg (33.2%) of *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (**19**); 134–168, 103 mg (20.5%) of *trans*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (**17**); 169–215, 121 mg (24.1%) of recovered 4-α-naphthyl-4-β-naphthyl-2-cyclohexenone (**7**); 281–401, 110 mg of a material shown by ^1H NMR to be a 3.8:1:2.6 mixture (11.2%, 2.9%, and 7.7%) of *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone

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

Table VI. Summary of Crystal Data and Intensity Collection Parameters for the Photoproducts of 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7)

parameter	bicyclic endo-β 19	bicyclic endo-α 17	3,4-enone 15	bicyclic exo-β 20	bicyclic exo-α 18
a (Å)	7.271	17.297	18.170	29.517	10.725
std dev	0.002	0.002	0.005	0.010	0.002
b (Å)	7.081	6.484	11.395	6.355	12.546
std dev	0.002	0.001	0.002	0.002	0.002
c (Å)	18.330	17.818	21.024	25.148	14.724
std dev	0.004	0.002	0.005	0.006	0.005
α (deg)	90.00	90.00	90.00	90.00	90.05
std dev	0.00	0.00	0.00	0.00	0.02
β (deg)	95.83	115.381	108.32	130.49	98.70
std dev	0.02	0.01	0.02	0.02	0.02
γ (deg)	90.00	90.00	90.00	90.00	110.19
std dev	0.00	0.00	0.00	0.00	0.02
V (Å^3)	939.0	1805.6	4132.1	3587.4	1835.1
molecules/cell (Z)	2	4	8	8	4
D_{calcd} (g/cm^3)	1.2323	1.2818	1.1202	1.2903	1.2612
temp (°C)	25	25	25	25	-30
space group	P_{2_1}	P_{2_1}	$P_{2_1/n}$	$C_{2/c}$	$P_{\bar{1}}$
μ, (mm^{-1})	0.07	0.55	0.48	0.07	0.03
radtn type	Mo-K$_\alpha$	Cu-K$_\alpha$	Cu-K$_\alpha$	Mo-K$_\alpha$	Mo-K$_\alpha$
scan mode	$\theta/2\theta$	ω	$\theta/2\theta$	ω	$\theta/2\theta$
2θ limits (deg)	3.5–45.0	4.0–115.0	4.0–115.0	3.0–45.0	3.5–45.0
min (h,k,l)	(-9,0,0)	(-19,0,0)	(-20,0,0)	(-28,0,0)	(-12,-14,0)
max (h,k,l)	(9,9,21)	(19,8,20)	(20,13,24)	(28,7,32)	(12,14,16)
scan range (deg)	0.9/0.8	0.9/0.9	0.6/0.6	1.2/1.4	0.9/0.9
reflctns measd	1511	3016	6693	5735	5481
unique reflctns	1395	2688	5664	2336	4837
obsd reflctns	1062	2446	3880	1160	4308
goodness of fit	2.3634	1.6088	1.8758	1.5008	7.8741
$R_1(F)$	0.037	0.038	0.075	0.040	0.058
$R_W(F)$	0.041	0.038	0.076	0.047	0.033

(18), *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (20), and 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (15), respectively. The cis bicyclics and 3,4-dinaphthyl enone were separated as described above, and all photoproducts were recrystallized as before.

All spectral data were identical with those found for the photoproducts of the direct photolysis (vide supra).

General Procedure for Single-Crystal X-ray Structure Determination. X-ray data were collected on either a Nicolet (Syntex) P-$\bar{1}$ or P3/F diffractometer for single crystals of each of the dinaphthyl enone photoproducts. Unit cell parameters were determined by least-squares refinement of 25 reflections from rotation photographs. Data were collected with 4 check reflections being monitored after every 50, and data having $F < 3\sigma(F)$ were rejected. Lorentz and polarization corrections were applied, and each structure was solved under appropriate space group symmetry by direct methods using SHELXS86[31] except for *exo*-6-α-naphthyl bicyclic 18 for which MULTAN80[32] was employed. Hydrogen atoms were located by difference Fourier synthesis, and full matrix least-squares refinement was carried out employing anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

X-ray quality single crystals of each of the photoproducts were prepared as follow: *endo*-6-β-naphthyl bicyclic 19 by slow crystallization from dichloromethane in methanol; *endo*-6-α-naphthyl bicyclic 17 by vapor diffusion of hexane into toluene; 3,4-dinaphthyl enone 15 by vapor diffusion of hexane into toluene; *exo*-6-β-naphthyl bicyclic 20 by slow crystallization from ether in hexane; *exo*-6-α-naphthyl bicyclic 18 by slow crystallization from dichloromethane in methanol. The results of the structure determinations are summarized in Table VI, and final parameters are available as supplementary material.

Exploratory Direct Photolysis of *trans*-5-α-Naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (19). A solution of 107 mg (0.307 mmol) of *trans*-5-α-naphthyl-6-β-naphthylbicyclo-[3.1.0]-2-hexanone (19) in 150 mL of benzene was photolyzed for 30 min, at which time ^{1}H NMR analysis of a 5.0-mL aliquot showed a 2:1.3:1 mixture of starting endo bicyclic 19, the *exo*-6-α-naphthyl bicyclic 20, and 3-α-naphthyl-4-β-naphthylcyclohexenone (15), respectively. Photolysis was continued for an additional 30 min, and concentration in vacuo yielded 101.4 mg of a pale yellow oil. The product was applied to a 20 × 20 cm preparative TLC plate and eluted 20 times with 40% dichloromethane in hexane to give the following: band 1, R_f = 0.35, 29.3 mg (27.4%) of starting *trans*-5-α-naphthyl-6-β-naphthylbicyclo-[3.1.0]-2-hexanone (19); 2, R_f = 0.25, 26.4 mg (24.7%) of *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]-2-hexanone (20); 3, R_f = 0.15, 31.7 mg (29.6%) of 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone (15).

The spectral data were identical with those observed for the corresponding products in the direct photolysis of the dinaphthyl enone (vide supra).

Exploratory Direct Photolysis of *trans*-5-β-Naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (17). A solution of 106 mg (0.303 mmol) of *trans*-5-β-naphthyl-6-α-naphthylbicyclo-[3.1.0]-2-hexanone (17) in 250 mL of benzene was photolyzed for 1 h. Concentration in vacuo yielded 107 mg of a pale yellow oil, which was subjected to preparative HPLC eluted with 70% dichloromethane in hexane to give the following: peak 1, R_f = 2.067 h, 52.3 mg (49.5%) of starting *trans*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (17); 2, R_f = 2.5 h, 51.5 mg (48.7%) of *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]-2-hexanone (18).

The spectral data were identical with those observed for the corresponding products in the direct photolysis of the dinaphthyl enone (vide supra).

3-β-Naphthyl-4-α-naphthyl-2-cyclohexenone (15). To a solution of 353 mg (1.70 mmol) of 2-bromonaphthalene in 15 mL of THF at -78 °C was added 1.15 mL (1.72 mmol) of 1.5 *M* *n*-butyllithium in hexane. After stirring for 15 min, 20 mg (0.793 mmol) of 6-α-naphthyl-3-methoxy-2-cyclohexenone[3g] in 5 mL of THF and 5 mL of anhydrous ether were added over 30 min. The solution was stirred for 1 h, warmed to room temperature, and quenched with 10% hydrochloric acid. The mixture was stirred at room temperature for 3 h, and basic workup of the organic phase yielded 563.4 mg of a yellow oil. The oil was applied to a 20 × 20 cm preparative TLC plate and eluted 5 times with 20% ether in hexane to give the following: band 1, R_f = 1.0, 175.6 mg of naphthalene; 2, R_f = 0.2, 76.4 mg of the 3,4-dinaphthyl enone. The 3-β-naphthyl-4-α-naphthyl-2-cyclohexenone was recrystallized from dichloromethane in hexane to give 53.6 mg (19.4%) of pale yellow needles, mp 79–80 °C.

The spectral data were identical with those of the 3,4-dinaphthyl enone observed in the direct photolysis of the 4,4-dinaphthyl enone (vide supra).

4-β-Naphthyl-1,3-cyclohexanedione (11a). To a 0 °C suspension of 3.00 g (0.0267 mol) of potassium *tert*-butoxide in 450 mL of anhydrous ether was added dropwise a solution of 5.35 g (0.0267 mol) of methyl 2-β-naphthylethanoate in 100 mL of ether. After stirring for 10 min, 0.26 g (0.95 mmol) of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was added, and then a solution of 2.40 mL (2.06 g, 0.029 mol) of methyl vinyl ketone in 50 mL of ether was added over 1 h. The suspension was stirred for 8 h at 0 °C, refluxed for 60 h, and then quenched with water. The aqueous phase was acidified to pH 3.0 (Congo Red) with 10% hydrochloric acid, and ether extraction followed by drying over magnesium sulfate and concentration in vacuo yielded 4.6 g (72%) of crude dione, mp 145–148 °C. Recrystallization from *p*-dioxane gave 2.35 g (36.9%) of white powder, mp 156 °C.

The spectral data for 4-β-naphthyl-1,3-cyclohexanedione were the following: IR (KBr) 3060, 3030, 2950, 2880, 2520 (OH), 1920, 1595 (C=O), 1510, 1458, 1429, 1353, 1337, 1272, 1225, 1207, 1086, 1048, 1030, 1009, 976, 928, 904, 869, 854, 831, 811, 758, 682, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.84 (m, 3 H, aryl), 7.70 (s, 0.14 H, enol aryl), 7.65 (s, 0.86 H, dione aryl), 7.49 (m, 2 H, aryl),

(31) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189.

(32) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368–376.

Table VII. Chemical Shifts of Nonaromatic Protons for 6-β-Naphthyl-3-methoxy-2-cyclohexenone (12) as a Function of Eu(fod)$_3$ Concentration

	[Eu(fod)$_3$] (mole fraction)					
proton	0.0	0.102	0.256	0.410	0.615	slope[a]
vinyl	5.58	6.48	7.8[b]	9.12	10.58	8.617
methoxy	3.76	3.80	3.86	3.92	3.98	0.383
methine	3.71	4.93	6.76	8.54	10.58	11.790
$COCH_2CH_2$	2.54	2.90	3.40	4.02	4.62	3.575
$COCH_2CH_2$	2.33	2.79	3.59	4.18	4.86	4.582

[a] Slope from plot of chemical shift as a function of Eu(fod)$_3$ concentration. [b] Estimated, obscured by aromatic peaks.

7.31 (m, 1 H, aryl), 5.688 (s, 0.14 H, vinyl), 3.956 (dd, J = 11.20, 5.80 Hz, 0.86 H, dione methine), 3.852 (dd, J = 8.37, 4.32 Hz, 0.14 H, enol methine), 3.629 (s, 1.72 H, dione C(O)CH_2C(O)), 2.818 (m, 1.72 H, dione CH_2CH_2), 2.414 (m, 2.46 H, dione CH_2CH_2 + enol OH + enol CH_2CH_2); MS m/e 238.0993 (calcd for $C_{16}H_{14}O_2$, m/e 238.0933).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.41; H, 5.89.

6-β-Naphthyl-3-methoxy-2-cyclohexenone (12) and 4-β-Naphthyl-3-methoxy-2-cyclohexenone (13). A solution of 1.0 g (4.20 mmol) of 4-β-naphthyl-1,3-cyclohexanedione (**11a**) and 0.25 g (1.45 mmol) of *p*-toluenesulfonic acid in 50 mL of methanol was refluxed for 5 h and concentrated in vacuo. Basic workup with ether gave 0.95 g of a colorless oil, which was shown by ^{1}H NMR to be a 1:1 mixture of the isomeric enol ethers. Chromatography on a 1.5 × 90 cm silica gel column eluted with 3.83 L of 5.0% and 7.52 L of 8.0% ethyl acetate in hexane, with 45-mL fractions being collected gave the following: fractions 115–183, 407.9 mg of the 6-β-naphthyl enol ether **12**; 184–252, 483 mg of the 4-β-naphthyl enol ether **13**. The 6-β-naphthyl-3-methoxy-2-cyclohexenone was recrystallized from dichloromethane in hexane to give 369 mg (34.9%) of white prisms, mp 133.5–134 °C. The 4-β-naphthyl-3-methoxy-2-cyclohexenone was recrystallized from dichloromethane in hexane to give 353.3 mg (33.5%) of white prisms, mp 120 °C.

The spectral data for 6-β-naphthyl-3-methoxy-2-cyclohexenone were the following: IR ($CHCl_3$) 3046, 2991, 2932, 1643 (C=O), 1606, 1505, 1461, 1451, 1440, 1433, 1382, 1351, 1321, 1247, 1224, 1193, 1168, 1001, 991, 854, 835, 919 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.78 (m, 3 H, aryl), 7.62 (s, 1 H, aryl), 7.45 (m, 2 H, aryl), 7.28 (m, 1 H, aryl), 5.585 (s, 1 H, vinyl), 3.760 (s, 3 H, methyl), 3.711 (t, J = 7.36 Hz, 1 H, methine), 2.54 (m, 2 H, CH_2CH_2), 2.35 (m, 2 H, CH_2CH_2); MS m/e 252.1151 (calcd for $C_{17}H_{16}O_2$, m/e 252.1150).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.09; H, 6.47.

The spectral data for 4-β-naphthyl-3-methoxy-2-cyclohexenone were the following: IR ($CHCl_3$) 3053, 2999, 2935, 1645 (C=O), 1608, 1510, 1453, 1382, 1150, 1227, 1191, 1172, 1004, 859, 843, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.80 (m, 3 H, aryl), 7.63 (s, 1 H, aryl), 7.49 (m, 2 H, aryl), 7.30 (m, 1 H, aryl), 5.677 (s, 1 H, vinyl), 3.948 (t, J = 4.46 Hz, 1 H, methine); 3.714 (s, 3 H, methyl), 2.39 (m, 3 H, CH_2CHH), 2.15 (m, 1 H, CH_2CHH); MS m/e 252.1151 (calcd for $C_{17}H_{16}O_2$, m/e 252.1150).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.66; H, 6.38.

The assignment of naphthyl regiochemistry was accomplished in a ^{1}H NMR shift reagent study of each of the isomers with tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)europium(III)[5a] (Eu(fod)$_3$). For the isomer identified as 6-β-naphthyl-3-methoxy-2-cyclohexenone (**12**), the 270-MHz ^{1}H NMR spectrum of a 0.0198 M solution of the enol ether in $CDCl_3$ containing Eu(fod)$_3$ in concentrations varying between 0.0 and 0.615 mole fraction was recorded. The resulting chemical shifts of the nonaromatic protons are tabulated in Table VII, along with the slopes resulting from a plot of chemical shift as a function of mole fraction of Eu(fod)$_3$ for each. An unusually large shift was also observed for 2 aromatic protons (slopes of 6.476 and 5.326, compared with the <0.1 slopes for all others), consistent with Eu(fod)$_3$ complexation at the neighboring carbonyl group. Significant nonlinearity was encountered above 0.615 mole fraction of Eu(fod)$_3$.

Table VIII. Chemical Shifts of Nonaromatic Protons for 4-β-Naphthyl-3-methoxy-2-cyclohexenone (13) as a Function of Eu(fod)$_3$ Concentration

	[Eu(fod)$_3$] (mole fraction)				
proton	0.0	0.166	0.333	0.499	slope[a]
vinyl	5.68	7.48	9.14	10.83	10.3
methoxy	3.71	3.97	4.19	4.43	1.4
methine	3.94	4.59	5.20	5.82	3.7
$COCH_2CH_2$	2.40	4.34	6.16	8.00	11.2
$COCH_2CH_2$	2.40	3.16	3.83	4.52	4.2

[a] Slope from plot of chemical shift as a function of Eu(fod)$_2$ concentration.

For the isomer identified as 4-β-naphthyl-3-methoxy-2-cyclohexenone (**13**), the 270-MHz ^{1}H NMR spectrum of a 0.0230 M solution of the enol ether in $CDCl_3$ containing Eu(fod)$_3$ in concentrations varying between 0.0 and 0.499 mole fraction was recorded. The resulting chemical shifts of the nonaromatic protons are tabulated in Table VIII, along with the slopes resulting from a plot of chemical shift as a function of mole fraction of Eu(fod)$_3$ for each. All aromatic protons showed slopes of less than 1. Significant nonlinearity was encountered above 0.499 mole fraction of Eu(fod)$_3$.

Hydrolysis of 4-β-Naphthyl-3-methoxy-2-cyclohexenone (13). A solution of 1.35 g (0.00533 mol) of 4-β-naphthyl-3-methoxy-2-cyclohexenone (**13**) and 60 mL of concentrated hydrochloric acid in 100 mL of THF was stirred at room temperature for 24 h. Basic workup with ether gave 1.13 g of 4-β-naphthyl-1,3-cyclohexanedione (**11a**), which was recrystallized from dichloromethane in hexane to give 0.906 g (71.2%) of the dione, mp 151–152 °C.

The spectral data were identical with those of the synthetic dione (vide supra).

3-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (14). To a solution of 0.56 mL (828 mg, 3.99 mmol) of 1-bromonaphthalene in 20 mL of THF at −78 °C was added 2.68 mL (4.02 mmol) of 1.5 M *n*-butyllithium in hexane. After stirring for 15 min, 510 mg (2.02 mmol) of 6-β-naphthyl-3-methoxy-2-cyclohexenone (**12**) in 40 mL of THF was added over 30 min. The solution was stirred for 1 h, warmed to room temperature, and quenched with 10% hydrochloric acid. The mixture was stirred at room temperature for 3.5 h, the layers were separated, and basic workup of the organic phase yielded 1.26 g of a yellow oil. The oil was chromatographed on a 1 × 80 cm silica gel column eluted with 855 mL of 2.5%, 2.05 L of 4.0%, and 1.35 L of 5.0% ethyl acetate in hexane, with 45-mL fractions being collected to give the following: fractions 11–20, 409.0 mg of naphthalene; 66–95, 234 mg of the 3,4-dinaphthyl enone. The 3-α-naphthyl-4-β-naphthyl-2-cyclohexenone was recrystallized from dichloromethane in hexane to give 126.4 mg (17.97%) of pale yellow needles, mp 121–122 °C.

The spectral data for 3-α-naphthyl-4-β-naphthyl-2-cyclohexenone were the following: IR (KBr) 3041, 2931, 2880, 1646 (C=O), 1602, 1510, 1380, 1361, 1350, 1311, 1240, 1211, 1200, 882, 861, 851, 823, 810, 797, 779, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.10 (d, J = 8.78 Hz, 1 H, aryl), 7.18–7.80 (m, 13 H, aryl), 6.508 (s, 1 H, vinyl), 4.431 (t, J = 4.2 Hz, 1 H, methine), 2.80 (m, 1 H, C(O)CH_2CHH), 2.65 (m, 1 H, C(O)$CHHCH_2$), 2.51 (m, 1 H, C(O)$CHHCH_2$), 2.31 (m, 1 H, C(O)CH_2CHH); MS m/e 348.1514 (calcd for $C_{26}H_{20}O$, m/e 348.1514).

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.08; H, 6.05.

Summary of Quantum Yield Results for 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7). All direct, sensitized, and quenched quantum yields were determined by using a microoptical bench[33] equipped with an Osram 200-W high pressure mercury lamp and a Bausch & Lomb Model 33-86-79 monochrometer. The monochrometer entrance and exit slits were set to 5.4 mm and 3.0 mm, respectively, giving a 21.8-nm band pass at peak half-height. Light output was measured by using digital electronic actinometry,[34] which was calibrated before and after each run with

(33) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.
(34) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weigt, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

Table IX. Final Quantum Yields for the Photoproducts of 4-α-Naphthyl-4-β-naphthyl-2-cyclohexenone (7)

product	quantum yield[a] direct[b]	aceto[c]	thiox[d]
endo-α-naphthyl bicyclic **17**	0.40	0.31	0.33
endo-β-naphthyl bicyclic **19**	0.35	0.38	0.39
3,4-dinaphthyl enone **15**	0.060	0.070	0.062
exo-β-naphthyl bicyclic **20**	0.046	0.050	0.045
exo-α-naphthyl bicyclic **18**	0.019	0.034	0.032

[a] Intercept of a plot of quantum yield as a function of percent conversion. Error ±10%, precision ±5%. [b] No additive, λ = 313 nm. [c] Acetophenone sensitized, λ = 334 nm. [d] Thioxanthone sensitized, λ = 366 nm.

potassium ferrioxalate chemical actinometry.[35]

Direct runs were made at 313 nm in 40.0 mL of benzene except for one low conversion control run at 366 nm, which yielded the same values. All sensitized and quenched runs were made in 27.0 mL of benzene. Quenched runs were irradiated at 313 nm, acetophenone runs at 334 nm, and thioxanthone runs at 366 nm. The solutions were purged with deoxygenated and dried nitrogen[30] for 1 h prior to and during photolysis. For runs made with 1,3-cyclohexadiene present, the quencher was not added until after the 1 h degassing period due to the volatility of the material.

Following photolysis, the solutions were concentrated in vacuo, and photoproducts were analyzed by using analytical HPLC, eluting with 8% ethyl acetate in hexane (50% saturated with water). Analyses were performed by the internal standard method, with 2-cyanonaphthalene being employed as a preeluting standard for direct runs and 1-phenyl-3-(*p*-methoxyphenyl)-3-cyano-1-propanone[36] being used as a post-eluting standard for sensitized and quenched runs. This change in standard was necessitated by interference in the analysis from the additives, but response factors were determined for all compounds relative to each standard. HPLC peaks were integrated with a Summagraphics Bitpad digitizer interfaced with a PDP-11/55 minicomputer.

In direct runs, the dinaphthyl enone concentration employed (ca. 0.002 M) resulted in absorption of greater than 99% of the incident light. In sensitized runs, the concentration of acetophenone or thioxanthone was selected to give minimally 99% absorption by the sensitizer. The dinaphthyl enone concentrations were sufficiently low (<0.005 M) as to preclude singlet energy transfer from the sensitizer (<1%). Alternatively, the enone concentrations were sufficiently high to ensure triplet energy transfer efficiencies of 90% from acetophenone (2×10^6 s^{-1} triplet decay rate[22]) and 99.9% from thioxanthone (1.3×10^4 s^{-1} triplet decay rate[7c]) in benzene (6×10^9 s^{-1} triplet energy transfer rate[7]).

The conditions employed in the determinations, the HPLC analytical results for each photoproduct, and the resulting quantum yields for each appear in Tables XLI, XLII, and XLIII in the supplementary material. The final quantum yields derived from the intercepts of plots of quantum yield as a function of conversion are tabulated in Table IX for the direct and sensitized runs.

Ultraviolet Absorption Studies. Ultraviolet–visible spectra were measured for the 4,4-dinaphthyl enone **7**, 2-methylnaphthalene, 1-methylnaphthalene, and 4,4-dimethyl-2-cyclohexenone in ethanol. The spectrum of the dinaphthyl enone was observed to be a linear combination of the absorptions of the methylnaphthalenes and the dimethyl enone. Further, at 313 nm the relative molar absorptivities of the dimethyl enone and 1-methylnaphthalene indicated that at least 95% of light at this wavelength will be absorbed by the naphthyl groups of dinaphthyl enone **7**. From similar considerations, at 366 nm essentially all light will be absorbed by the enone chromophore.

Phosphorescence and Fluorescence Emission Measurements. All emission spectra were recorded on an Aminco-Keirs spectrophosphorimeter equipped with an Hanovia 901C-1 150-W Xenon arc lamp, internal baffles to eliminate scatter, and an interface for data collection with a Digital PDP-11/55 minicomputer. An excitation wavelength of 265 nm was used for all measurements, with emission wavelengths in the range 200–800 nm being scanned. Samples were dissolved in 4:1 methylcyclohexane/2-methylbutane, with concentrations of 10^{-4} M being employed to achieve optical densities of 0.5–0.8 and minimize scatter. All samples were thoroughly deoxygenated by 5 freeze–pump–thaw cycles prior to recording of the spectra.

Phosphorescence measurements were made at 77 K on samples of both naphthalene and the dinaphthyl enone **7**. The naphthalene emission was highly structured and showed a 0–0 band at 476 nm, while the enone's was unresolved with a 0–0 band at 477 nm. The emission intensities of the two compounds were comparable. Fluorescence measurements were made at 295 K. Naphthalene showed strong emission with a 0–0 band at 311 nm, however no enone fluorescence could be detected under identical conditions. This places an upper limit on the intensity of dinaphthyl enone emission at 10^{-3} times that of naphthalene.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with the MMP2 program of Allinger.[24] During geometry optimization it was necessary to constrain the α-naphthyl group to be planar in order to avoid severe distortions from planarity. No such problems were encountered for the β-naphthyl group.

For conformations of the starting dinaphthyl enone **7**, minima were located by naphthyl rotations. For either α-naphthyl or β-naphthyl axial, the lowest energy conformer (**7-B-α** and **7-A-β**) had the axial group's π-system oriented perpendicular to the enone π-system. The second lowest energy conformer for each (**7-A-α** and **7-B-β**) had the π-systems of the axial group and the enone oriented towards each other. A 180° rotation of the β-naphthyl group in any of these conformations resulted in a conformer of equal energy, within 0.2 kcal/mol. The MMP2 steric energy for each of the conformations is shown in Table X, along with the dihedral angle between the axial naphthyl group and the enone system.

Table X. MMP2 Steric Energies of Dinaphthyl Enone 7 Conformations

conformer	axial group	angle,[a] deg	MMP2, energy, kcal/mol
	Conformational Minima		
7-A-β	β-naphthyl	13.3	−5.136
7-B-α	α-naphthyl	16.1	−4.655
7-B-β	β-naphthyl	113.5	−2.521
7-A-α	α-naphthyl	102.1	−1.494
	Naphthyl Rotation Transition States		
α-Int	α-naphthyl	56.7	8.060
β-Int	β-naphthyl	34.5	2.183

[a] Dihedral angle between the plane of the axial naphthyl group and the bond between C-4 and C-3 of the cyclohexenone. For a perpendicular orientation of enone and naphthyl π-systems, this angle is 0°. When the π-systems are aimed toward one another, the angle is 90°.

The transition state for axial naphthyl rotation from a perpendicular to an overlapping conformation was modeled for either α-naphthyl or β-naphthyl axial. Here the axial naphthyl group was constrained to be coplanar with the bond between C-4 of the cyclohexenone and the equatorial naphthyl group. The MMP2 steric energy of the transition structure for each of the naphthyl groups axial is included in Table X.

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Appendix

Derivation of Limits for Excitation Partitioning between Two Noninterconverting Excited States. If a molecule possesses 2 excited states A and B which do not interconvert, the total light (I) absorbed by the molecule may be partitioned between the two states (F_A

(35) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.
(36) Unpublished results of H. E. Zimmerman and T. P. Cutler.

$= I_A/I$ and $F_B = I_B/I$). The observed efficiency for reaction of A or B will be the true rearrangement quantum yield (i.e., the ϕ^0's) multiplied by the fraction of light reaching that state:

$$\phi_A = \phi_A^0 F_A \quad (8a)$$

$$\phi_B = \phi_B^0 F_B \quad (8b)$$

Rearranging gives expressions for the true quantum yields:

$$\phi_A^0 = \phi_A/F_A \quad (9a)$$

$$\phi_B^0 = \phi_B/F_B \quad (9b)$$

An upper limit on the magnitude of the quantities in eq 9 exists since by definition, the quantum yield of a nonchain unimolecular process cannot exceed 1.0:

$$\phi_A^0 \leq 1.0 \quad (10a)$$

$$\phi_B^0 \leq 1.0 \quad (10b)$$

and therefore

$$\phi_A/F_A \leq 1.0 \quad (11a)$$

$$\phi_B/F_B \leq 1.0 \quad (11b)$$

Thus a lower limit on F_A and F_B is obtained by simple cross-multiplication:

$$\phi_A \leq F_A \quad (12a)$$

$$\phi_B \leq F_B \quad (12b)$$

This result is entirely reasonable, since at least as much excitation must reach each group as is utilized in its reaction.

An upper limit on the magnitudes of F_A and F_B results from the fact that the total fraction of light in A and B cannot exceed 1.0:

$$F_A + F_B \leq 1.0 \quad (13)$$

and thus by simple subtraction:

$$F_A \leq (1 - F_B) \quad (14a)$$

$$F_B \leq (1 - F_A) \quad (14b)$$

Now, if each side of eq 12b is subtracted from 1.0, and each side of eq 12a is subtracted from 1.0, the inequalities 15 are obtained:

$$(1 - F_B) \leq (1 - \phi_B) \quad (15a)$$

$$(1 - F_A) \leq (1 - \phi_A) \quad (15b)$$

With reference to eq 14a and 15a, it is clear that since F_A is less than $(1 - F_B)$, and $(1 - F_B)$ is itself less than $(1 - \phi_B(\text{obs}))$, F_A must also be less than $(1 - \phi_B(\text{obs}))$. Equations 14b and 15b give a similar result for F_B, and thus upper limits may be placed as follow:

$$F_A \leq (1 - \phi_B) \quad (16a)$$

$$F_B \leq (1 - \phi_A) \quad (16b)$$

In this way eq 12 and 16 place limits on the fraction of excitation reaching each of excited states A and B.

Registry No. 7, 118890-23-6; 8, 91879-84-4; 9, 118868-36-3; 11a, 118868-35-2; 12, 118868-37-4; 13, 118868-38-5; 14, 118868-39-6; 15, 118868-40-9; 17, 118868-41-0; 18, 118868-42-1; 19, 118868-43-2; 20, 118868-44-3; $Eu(FOD)_3$, 17631-68-4; methyl vinyl ketone, 78-94-4; 6-α-naphthyl-3-methoxy-2-cyclohexenone, 98585-94-5; 2-bromonaphthalene, 580-13-2; methyl 2-β-naphthylethanoate, 2876-71-3; 1-bromonaphthalene, 90-11-9.

Supplementary Material Available: ORTEP drawings and tables of positional parameters, interatomic distances, bond angles, and temperature factors for compounds 15, 17, 18, 19, and 20 and tables of conditions and HPLC results for quantum yield determinations of 7 (39 pages). Ordering information is given on any current masthead page.

Hydrolysis of the Vinyl Ether Functional Group in a Model for Prostacyclin in Which the Carboxyl Group Has Been Replaced by a Pyridine Ring

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The hydrolysis of the vinyl ether functional group in the three isomeric compounds (*Z*,*E*)-2-methoxy-6-(2-pyridyl)hex-2-ene (3 and 4) and 2-methoxy-6-(2-pyridyl)hex-1-ene (5) has been studied in hydrochloric acid solutions and acetic acid and biphosphate ion buffer solutions. The rate constant ratio for the hydronium ion catalysis of the neutral and positive forms of the substrates are 45.7, 44.9 and 15.7, respectively. The rate accelerations are interpreted in terms of intramolecular general acid catalysis and the results are discussed in relation to the suggested mechanism for hydrolysis of prostacyclin.

The unusual high hydrolytic lability of prostacyclin (1)[1] has been traced to its carboxylic acid functional group acting in ionized form.[2] Two mechanistic alternatives, illustrated in Scheme I, have been discussed for the hydrolysis reaction of prostacyclin.[2-4]

Mechanism 1 is an electrostatic catalysis[5] by the carboxylate ion during intermolecular protonation. The negative charge on the carboxylate group can stabilize the developing positive charge on the vinyl ether function in the transition state, TS1. In mechanism 2, there is a rapid

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(4) Bergman, N.-Å.; Jansson, M.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1988**, *53*, 2544.
(5) This is strictly speaking a field effect but the term electrostatic catalysis has been kept here as this terminology has been used in related work.[2-4] The inductive effect is probably negligible in the present system.

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