1275, 1115, 1015 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.91 (t, J = 7 Hz, 3 H), 1.34–1.88 (m, 10 H), 2.45 (s, 1 H), 3.44–3.56 (m, 1 H), 3.92–4.02 (m, 1 H), 4.15 (s, 3 H), 4.29 (dd, J = 7, 7 Hz, 1 H), 4.75 (brd, J = 7 Hz, 1 H), 6.94 (d, J = 9 Hz, 1 H), 7.27 (d, J = 8 Hz, 1 H), 7.55 (dd, J = 9, 8 Hz, 1 H); mass spectrum, *m/e* (relative intensity) EI 344 (M$^+$, 1), 260 (35), 242 (40), 227 (25), 213 (90), 85 (100); exact mass calcd for $C_{20}H_{24}O_5$ 344.1628, found 344.1623.

1-Methoxy-5-(2-propenyloxy)-5-[3-(tetrahydropyran-2-yloxy)hexyn-1-yl]benzocyclobuten-6-one, 21. Two diastereomers of the title compound were obtained when **16** was allylated by using the procedure described for the synthesis of **19b**. Diastereomer 1 (major): light yellow oil (0.27 g, 0.70 mmol), 73% yield); IR (CCl$_4$) 3075, 3015, 1775, 1600, 1565, 1480, 1435, 1275, 1115, 1020, 980, 920 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.94 (t, J = 7 Hz, 3 H), 1.43–1.88 (m, 10 H), 3.46–3.56 (m, 1 H), 3.72–3.83 (m, 1 H), 4.15 (s, 3 H), 4.38 (brd, J = 6 Hz, 2 H), 4.52 (dd, J = 7, 7 Hz, 1 H), 4.87–4.95 (m, 1 H), 5.20 (dd, J = 11, 2 Hz, 1 H), 5.32 (dd, J = 18, 2 Hz, 1 H), 5.97 (ddd, J = 18, 11, 7 Hz, 1 H), 6.96 (d, J = 8 Hz, 1 H), 7.24 (d, J = 8 Hz, 1 H), 7.56 (dd, J = 8, 8 Hz, 1 H); mass spectrum, *m/e* (relative intensity) EI 384 (M$^+$, 1), 300 (25), 259 (45), 203 (45), 85 (100); exact mass calcd for $C_{23}H_{28}O_5$ 384.1936, found 384.1943. Diastereomer 2 (minor): light yellow oil; IR (CCl$_4$) 3075, 3015, 1775, 1605, 1570, 1485, 1435, 1280, 1120, 1020, 920 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.92 (t, J = 7 Hz, 3 H), 1.38–1.90 (m, 10 H), 3.44–3.55 (m, 1 H), 3.88–4.01 (m, 1 H), 4.13 (s, 3 H), 4.34 (dd, J = 8, 8 Hz, 1 H), 4.41 (d, J = 7 Hz, 2 H), 4.76 (dd, J = 11, 2 Hz, 1 H), 5.19 (dd, J = 11, 2 Hz, 1 H), 5.31 (dd, J = 18, 2 Hz, 1 H), 5.98 (ddd, J = 18, 11, 7 Hz, 1 H), 6.94 (d, J = 9 Hz, 1 H), 7.23 (d, J = 8 Hz, 1 H), 7.54 (dd, J = 9, 8 Hz, 1 H); mass spectrum, *m/e* (relative intensity) EI 384 (M$^+$, 8), 300 (6), 259 (35), 203 (40), 85 (100); exact mass calcd for $C_{23}H_{28}O_5$ 384.1936, found 384.1934.

5-Methoxy-2-(2-propenyl)-3-[1-(tetrahydropyran-2-yloxy)butyl]-naphthalene-1,4-dione. When the major diastereomer (0.206 g, 0.54 mmol) of the above was subjected to thermolysis in refluxing *p*-xylene for 3 h, the title compound was obtained as a light yellow oil in 74% yield after chromatographic purification on silica gel with 4:1 hexanes/ethyl acetate as the eluting solvent: IR (CCl$_4$) 3070, 1660, 1585, 1275, 1255, 1067, 1030, 965, 905 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.97 (t, J = 7 Hz, 3 H), 1.30–1.90 (m, 10 H), 3.47–3.58 (m, 1 H), 3.59 (dd, J = 14, 6 Hz, 1 H), 3.76 (dd, J = 14, 6 Hz, 1 H), 3.84–3.94 (m, 1 H), 3.99 (s, 3 H), 4.45–4.51 (m, 1 H), 5.06 (d, J = 11 Hz, 1 H), 5.07 (d, J = 17 Hz, 1 H), 5.89 (dddd, J = 17, 11, 6, 6 Hz, 1 H), 7.27 (d, J = 9 Hz, 1 H), 7.64 (dd, J = 9, 8 Hz, 1 H); mass spectrum, *m/e* (relative intensity) EI 384 (M$^+$, 8), 343 (10), 300 (35), 282 (25), 257 (23), 239 (15), 85 (100); exact mass calcd for $C_{23}H_{28}O_5$ 384.1938, found 384.1952. Thermolysis of the minor diastereomer of the cyclobutenone gave an isomer of the above naphthoquinone in 55% yield.

3-(1-Hydroxybutyl)-5-methoxy-2-(2-propenyl)-1,4-naphthalenedione, 16b. The above major diastereomer (0.134 g, 35 mmol) was hydrolyzed as described for the conversion of **20** to **16a**. This gave the naphthoquinone **16b** in 51% yield as a yellow oil after chromatography on silica gel with hexanes/ethyl acetate as the eluting solvent (7:3). In a similar fashion the minor diastereomer was converted to **16b** in 64% yield: IR (CCl$_4$) 3550, 3070, 2965, 2885, 2840, 1650, 1620, 1590, 1470, 1280, 1075, 975, 910 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.95 (t, J = 7 Hz, 3 H), 1.32–1.50 (m, 1 H), 1.56–1.70 (m, 2 H), 1.97–2.04 (m, 1 H), 3.36 (dd, J = 14, 6 Hz, 1 H), 3.43 (dd, J = 14, 6 Hz, 1 H), 3.77 (d, J = 11 Hz, 1 H), 4.02 (s, 3 H), 4.72 (ddd, J = 11, 10, 4 Hz, 1 H), 5.10 (dd, J = 11, 2 Hz, 1 H), 5.13 (dd, J = 18, 2, Hz, 1 H), 5.83 (dddd, J = 18, 11, 6, 6 Hz, 1 H), 7.29 (d, J = 8 Hz, 1 H), 7.67 (dd, J = 8, 8 Hz, 1 H), 7.75 (d, J = 8 Hz, 1 H). These data are in excellent agreement with those reported for the known compound.[14]

Acknowledgment. We thank the National Institutes of Health (CA-11890 and GM-36312) for financial support of this work.

Photochemical Rearrangements of Molecules Having Quenchers on a Chain. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: The photochemistry of 4,4-diphenylcyclohexenones bearing substituents at C-6 was investigated. The C-6 substituents utilized were 4-(β-naphthyl)butyl, β-naphthylmethyl, biphenylylmethyl, methyl, and propyl. There was an interesting kinetic preference for formation of that C-3 substituted *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one stereoisomer with the 3-endo alkyl configuration. This stereoselectivity was understood on the basis of the geometry of the partially phenyl-migrated species. The naphthylbutyl enone had a direct irradiation quantum yield that was essentially that (0.048) of the unsubstituted 4,4-diphenylcyclohexenone as well as the methyl and propyl enones. In contrast, the naphthylmethyl enone efficiency was markedly depressed (0.0059). In both naphthylalkyl enones, singlet excitation was distributed with facility from naphthyl to enone with triplet excitation being then engendered by intersystem crossing at the locus of the carbon groups. In contrast, enone to naphthyl triplet energy transfer occurred in the naphthylmethyl but not the naphthylbutyl enone. The efficiency of the biphenylylmethyl enone is also reported (0.033). In sensitized runs the naphthyl moiety was able to intercept sensitizer species and prevent reaction to varying extents. In the naphthylbutyl case, approximately half of the sensitizer triplets were intercepted and quenched. In the naphthylmethyl case, interception was more efficient ($\geq$75%). Moreover in this case, T_1, with the naphthyl group excited, was able to afford to the extent of 24% the reactive T_2 in which the enone moiety was excited. Finally, in an approach to placing triplet enone reaction rate determination on a firmer basis, a viscosity-dependent Stern–Volmer treatment was employed.

Two and a half decades ago we reported a photochemical reaction in which a 4-aryl-substituted cyclohexenone rearranged to a 6-arylbicyclo[3.1.0]hexan-2-one.[3a] Subsequently we found the rearrangement to proceed via the enone triplet excited state

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(1) This is Paper 154 of our photochemical series and Paper 214 of the general series.

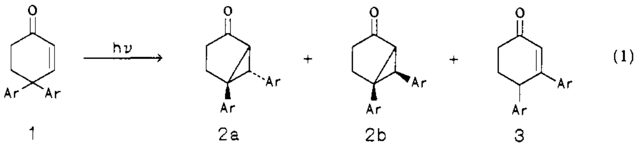
(2) For Paper 153 see: Zimmerman, H. E.; Nuss, J. M.; Tantillo, A. W. *J. Org. Chem.* **1988**, *53*, 3792–3803.

0002-7863/89/1511-0995$01.50/0

Table I. Photoproduct Endo:Exo Product Ratios

reactant	substituent	products (endo, exo)	endo:exo ratio
6	β-naphthylbutyl	**12a**, **12b**	1.7
7	β-naphthylmethyl	**13a**, **13b**	1.8
8	biphenylylmethyl	**14a**, **14b**	1.4
9	methyl	**15a**, **15b**	3.8
10	propyl	**16a**, **16b**	1.6

and determined its efficiency and reaction rate.[3b] Further studies investigated migratory aptitudes[3c,d] and revealed an activation barrier for the triplet rearrangement.[3e] Very recent efforts dealt with bichromophoric molecules in which di-π-methane and 4-aryl enone rearrangements competed.[3f,g] The 4-arylcyclohexenone rearrangement is depicted in eq 1.

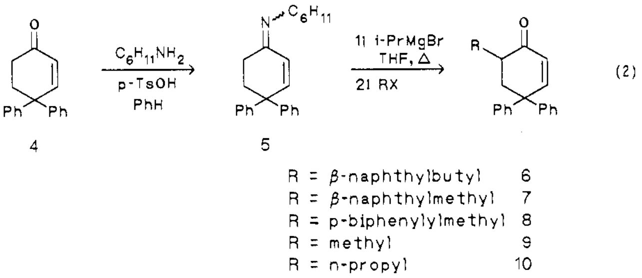


Our continuing endeavors in the realm of enone photochemistry required an enone reactant possessing a side chain bearing a moiety that would be a quencher if it were a separate, external molecule. We were interested in the ability of such an intramolecular moiety at the end of a chain to quench the enone rearrangement. Additionally, we wished to investigate the ability of such an enone possessing a quencher side chain to intercept an external sensitizer molecule. Finally, we were concerned with a difficulty inherent in the determination of triplet reaction rates. Thus, most commonly one needs to assume a value for the rate of quenching, an approach we hoped to avoid.

We began this study with the 4,4-diphenylcyclohexenone system substituted at carbon-6 with β-naphthylbutyl, β-naphthylmethyl, and p-biphenylylmethyl groups.

Results

Synthesis of Photochemical Reactants of Interest. The C-6 substituted diphenyl enones were most conveniently synthesized by the method of Stork and Dowd[4] as applied to cyclohexenones.[5] Note eq 2. Also included are enones **9** and **10** employed for control purposes and having C-6 methyl and propyl substituents.



Exploratory Cyclohexenone Photochemistry. The five C-6 substituted cyclohexenones **6–10** were subjected to preparative irradiation in benzene with a sodium metavanadate filter solution cutting off light below 340 nm. In each case, two products were obtained. The NMR spectra were reminiscent of the parent *trans*-5,6-diphenylbicyclo[3.1.0]hexanone (**11**) and its aryl relatives.[3f,g] These have an AB quartet with characteristic coupling of 9.5–10 Hz due to the cis cyclopropyl methines (vs 3–4.5 Hz for trans). Thus it seemed that the two compounds isolated were C-3 epimers (note bicyclic numbering in eq 3), both with the phenyl groups trans. This structural assignment was confirmed by synthesis (vide infra). The very minor photoproducts of our previous study[3b] (note **2b** and **3** in eq 1) were not detected. Hence the overall photoreaction may be depicted as in eq 3.

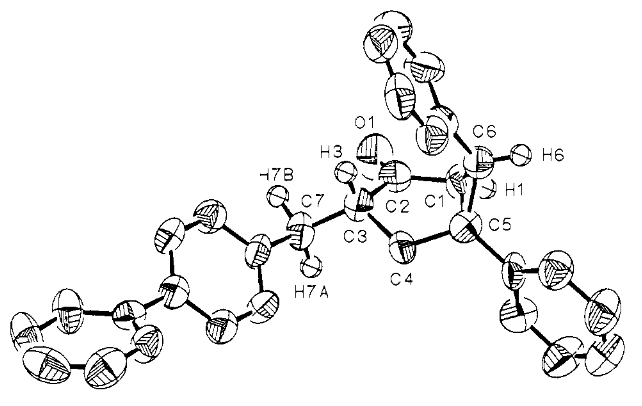
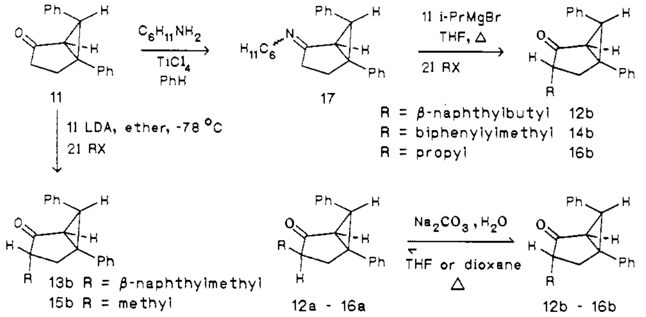
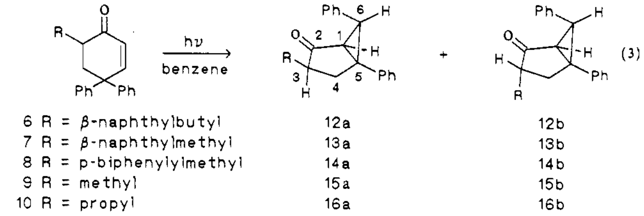


Figure 1. X-ray structure of *exo*-biphenylylmethyl photoproduct.

Scheme I. Synthesis of Photoproducts and Observation of Their Epimerization





A particularly interesting point was the observation that in every instance the 3-endo epimer was formed in preference to the 3-exo stereoisomer. Table I lists the stereoisomer endo:exo product ratios. That these ratios represent kinetic distributions is clear, first from the exclusion of light absorbed by the photoproducts and second from the observation of constant ratios with varying extents of reaction.

Xanthone sensitization of the two naphthyl-substituted enones **6** and **7**, using the metavanadate filter and sufficient sensitizer to absorb essentially all the incident light, gave the same product distribution as in the direct runs giving evidence for triplet multiplicity of the reactions.

Synthesis, Epimerization, and Structure Proof of the Photoproducts. The exo photoproduct structures were established securely by independent[6] synthesis. Note Scheme I. The alkylations of the bicyclic enolate and also the imine conjugate base led with total stereoselectivity[7] to the 3-exo epimers, **12b** through **16b**, as

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(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.

(4) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178–2180.

(5) Zimmerman, H. E.; Albrecht, F. X.; Haire, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 3726–3740.

(6) (a) Compare footnote 12 of ref 6b. (b) Zimmerman, H. E.; Tolbert, L. M. *J. Am. Chem. Soc.* **1975**, *97*, 5497–5507.

(7) (a) We use the term "stereoselective" here in accord with the most commonly accepted usage.[7b,c] (b) Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108–116. (c) Eliel, E. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962.

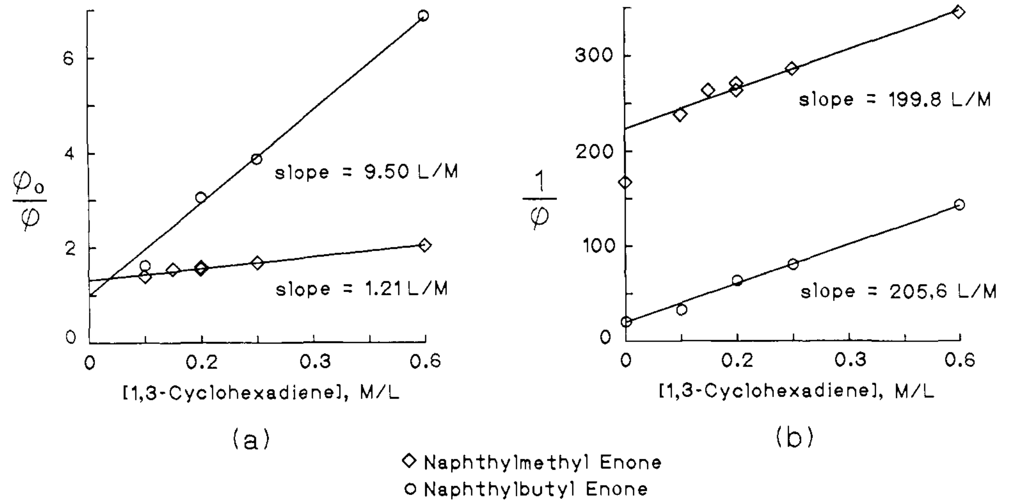

Figure 2. (a) Stern–Volmer plot of ϕ_0/ϕ versus quencher concentration. (b) Stern–Volmer plot of $1/\phi$ versus quencher concentration.

would be anticipated from least hindered approach considerations. The exo assignment to the minor isomers formed in the photochemistry was confirmed by X-ray structure determination of the 3-*exo*-(biphenylylmethyl)bicyclohexanone **14b** whose NMR spectrum was typical of the entire 3-exo series. An Ortep drawing is presented in Figure 1.

In each case the major endo photoproduct proved susceptible to epimerization under mild, sodium carbonate–THF–water (or sodium carbonate–dioxane–water) conditions to afford the corresponding minor exo photoproduct. Inspection of models (e.g. note Figure 1), consideration of interactions between *endo*-phenyl and C-3 substituents, and calculations to be discussed later all supported our assignment of the stable isomer having the C-3 substituent exo. The bicyclic compounds having an *endo*-methyl or methylene characteristically exhibited a high-field NMR peak at δ 0.7–0.9, suggesting shielding by the face of the endo phenyl group.

Quantum Yield Determinations of the Substituted Cyclohexenones. Quantum yields were determined with use of the semimicro optical bench apparatus previously described[8] along with an electronic actinometer.[9] Each set of runs was calibrated with the usual ferrioxalate actinometry.[10] The quantum yields are summarized in Table II.[14a] These values may be considered to be extrapolated to 0% conversion, since the efficiencies were found to be independent of extent of reaction in the 1 to 5% conversion range employed and, as noted in connection with the reaction stereochemistry, the photoproducts did not absorb at the irradiation wavelength of 366 nm used most often.

Sensitized runs were made with xanthone (E_T = 74 kcal/mol[11a]), thioxanthone (E_T = 66 kcal/mol[11b]), and acetophenone (E_T = 74 kcal/mol[11c]). These were selected in view of the 69 kcal/mol spectroscopic triplet energy[12] of the parent enone **1** and that of 61 kcal/mol[13] for naphthalene. These runs are included in Table II.[14b]

Table II. Quantum Yields of Substituted Cyclohexenones[a]

reactant	additive	endo epimer	exo epimer	total[c]
parent enone **1**[b]	none	*f*	*f*	0.043
parent enone **1**[b]	benzophenone	*f*	*f*	0.015
parent enone **1**[b]	acetophenone	*f*	*f*	0.036
parent enone **1**[b]	propiophenone	*f*	*f*	0.038
naphthylbutyl enone **6**	none	0.029	0.017	0.048
naphthylbutyl enone **6**	none[d]	0.031	0.020	0.051
naphthylbutyl enone **6**	xanthone	0.014	0.009	0.023
naphthylmethyl enone **7**	none	0.0038	0.0021	0.0059
naphthylmethyl enone **7**	none[d]	0.0037	0.0022	0.0059
naphthylmethyl enone **7**	xanthone	0.0011	0.0006	0.0017
naphthylmethyl enone **7**	thioxanthone	0.0012	0.0006	0.0018
biphenylylmethyl enone **8**	none	0.019	0.014	0.033
biphenylylmethyl enone **8**	acetophenone[e]	0.007	0.005	0.012
methyl enone **9**	none	0.0040	0.010	0.050
propyl enone **10**	none	0.029	0.018	0.047
propyl enone **10**	xanthone	0.026	0.015	0.041

[a] Irradiations at 366 nm unless noted. [b] Data taken from ref 3b. [c] Error of ±10%. [d] Irradiation at 313 nm. [e] Irradiation at 340 nm. [f] Not applicable.

Intramolecular Quenching of Naphthyl Singlets and Fluorescence. With the objective of determining interactions between the unexcited enone and excited naphthyl chromophores in the singlet of the naphthylbutyl and naphthylmethyl enones **6** and

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(8) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

(9) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

(10) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.

(11) (a) Pownall, H. J.; Huber, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6429–6436. (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777. (c) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbury, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468. (d) Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4230–4238. (e) Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4781–4782.

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

(13) (a) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1965. (b) Marichetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768–777. (c) Terenen, A.; Ermolaev, V. *Trans. Faraday Soc.* **1952**, *52*, 1043–1052.

(14) (a) The enone concentrations employed (<0.01 M) were low enough so that intermolecular triplet quenching of the naphthylalkyl enones by another enone molecule was not efficient (<2%). The extinction coefficients (ϵ) of the naphthyl and enone chromophores at 313 nm are ca. 300 and 200 L·M^{-1}·cm^{-1}, respectively. Upon 313-nm irradiation 60% of the light is absorbed by the naphthyl chromophore. At 366 nm, the naphthyl group does not absorb ($\epsilon < 0.1$) and the enone moiety (ϵ ca. 20) absorbs all of the light. (b) In each run the relative concentrations of sensitizer and photoreactant enone were selected to give minimally 99% absorption by the sensitizer. The enone concentrations employed, ca. 0.005 M, were sufficiently low as to preclude singlet energy transfer (<1%). The triplet decay rates for xanthone, thioxanthone, and acetophenone are reported to be 2×10^4,[11a] 1.3×10^4,[11b] and 2×10^6 s^{-1},[11c] respectively. Thus, with a bimolecular rate of exothermic triplet energy transfer for aromatic ketones of 6×10^9 L·M^{-1}·s^{-1} in benzene,[15] the enone concentrations used were sufficiently high to ensure that the rate of energy transfer from the sensitizer to enone was greater than the triplet decay of the sensitizer, i.e., a sensitization efficiency of greater than 99% for xanthone and thioxanthone and 90% for acetophenone.

(15) (a) A value of 5×10^9 L·M^{-1}·s^{-1} for the rate of triplet quenching in benzene has been measured.[11b] (b) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 1245–1251. (c) Wagner, P. J.; Spoerke, R. W. *Ibid.* **1969**, *91*, 4437–4440. (d) Scaiano et al. (Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *Ibid.* **1984**, *106*, 1539–1542) have reported a value of 6×10^9 L·M^{-1}·s^{-1} for the quenching of *p*-methoxyacetophenone by oxygen in benzene and similar values for analogous quenching of various ketones by dienes in this solvent.

(16) For the naphthylmethyl enone the slope of the ϕ_0/ϕ versus [Q] plot is equal to $(k_q\tau)b$, where b is the intercept. In addition the slope of the $1/\phi$ versus [Q] plot is defined as usual (k_q/k_r). See Supplemental Material for derivation.

7, several tests were made. First, equimolar mixtures of β-methylnaphthalene and 4,4-diphenylcyclohexenone (**4**) showed both normal ultraviolet absorption and normal naphthyl fluorescence emission spectra over reasonable[6b] concentration ranges. Second, the fluorescence emission behavior of the naphthylbutyl and naphthylmethyl enones was studied. In contrast to the solutions of the mixtures no detectable emission was observed. Hence there is evidence for intramolecular quenching of the naphthyl singlet by energy transfer to the enone moiety.

Determination of Stern–Volmer Slopes. In order to determine an excited state triplet rearrangement rate, one needs to obtain the $k_q\tau$ value from a Stern–Volmer treatment. Quenching studies were carried out on the naphthylbutyl and naphthylmethyl cyclohexenones **6** and **7**, respectively, using cyclohexadiene (E_T = 53 kcal/mol[11d,e]). The data are plotted in Stern–Volmer form in Figures 2a,b, and the slopes obtained are included. Reference to the ϕ_0/ϕ versus [Q] plot (Figure 2a) shows that the intercept for naphthylmethyl enone **7** is not unity, a result suggestive of quenching of two excited states, a short-lived enone triplet and a long-lived naphthyl triplet (vide infra).

The Stern–Volmer treatment affords a slope of $k_q\tau$. Hence, if one knows k_q, one can obtain the lifetime τ and thus its inverse, the total rate of decay $k_{d(tot)}$. With this information, the rate of triplet reaction, k_r, is readily derivable from the relation $k_r = \phi k_{d(tot)}$.

Quenching Dependence on Viscosity. Hitherto, with a Stern–Volmer plot in hand, we have used the rate of diffusion, as calculated from the Debye equation,[17] as the value of k_q, the rate of quenching. However, more recently there has been evidence that rates of quenching are sometimes less than diffusion controlled.[18]

Thus, in the present study an independent determination of the rate of quenching of 4,4-diphenylcyclohexenones (note eq 4a) was needed. However, eq 4a is an overall, operational statement, and quenching is better depicted in detail as in eq 4b.[19a] Here $^3(E^*{\cdot}Q)$ is a triplet encounter pair. In absence of either reversibility in quenching or static quenching effects at high concentration, k_q is given by eq 5.[19a–c] It is seen that, unless the rate of diffusion, k_{dif}, is rate-limiting and $k_{ET} \gg k_{-dif}$, the rate of diffusion (k_{dif}) gives only an upper limit to the effective rate of quenching (k_q).

$$^3E^* + Q \xrightarrow{k_q} E + {}^3Q^* \qquad (4a)$$

$$E \xrightarrow{h\nu} {}^3E^* + Q \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} {}^3(E^*{\cdot}Q) \xrightarrow{k_{ET}} E + {}^3Q^* \qquad (4b)$$

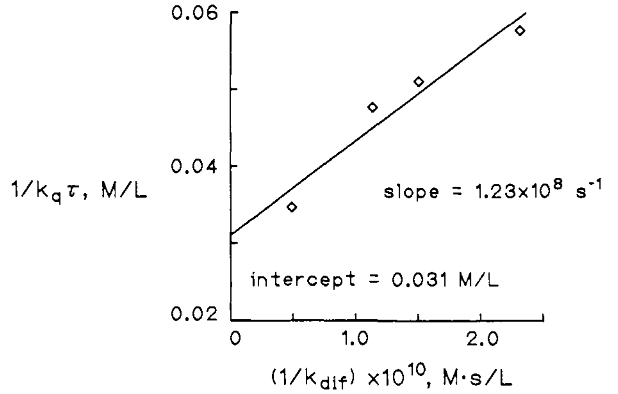

Figure 3. Plot of $1/k_q\tau$ versus $1/k_{dif}$.

Table III. Quenching Rates for Diphenyl Enone **4** by Cyclohexadiene in Various Solvents

			rate constants × 10^{-10} L·M^{-1}·s^{-1}		
solvent	viscosity[a]	$k_q\tau$, L·M^{-1}	k_{dif}[b]	k_q[c]	k_q[d]
n-hexane	0.313	28.8	2.06	0.31	0.57
methylcyclohexane	0.734	21.0	0.88	0.26	0.41
cyclohexane	0.980	19.6	0.66	0.24	0.33
n-dodecane	1.508	17.3	0.43	0.20	0.33
benzene	0.652	11.3[e]	1.00	0.27	0.35

[a] Values at 20 °C in units of cP taken from ref 17c. [b] Calculated from the Debye equation, ref 17a. [c] Rate constants obtained from the data analysis discussed above. [d] Rate constants obtained from the alternative treatment of Saltiel presented in the Experimental Section; see ref 18b,c. [e] Value determined in previous study, ref 3b.

$$k_q = (k_{dif}k_{ET})/(k_{-dif} + k_{ET}) \qquad (5)$$

The evaluation of k_q was accomplished by determining the efficiency of quenching the parent enone **4** triplet as a function of solvent viscosity. To this end we determined $k_q\tau$, using Stern–Volmer methodology, in hexane (η = 0.313 cP), methylcyclohexane (η = 0.734 cP), cyclohexane (η = 0.980 cP), and *n*-dodecane (η = 1.508 cP). Details are given in the Experimental Section.

A plot of $1/k_q\tau$ vs $1/k_{dif}$ was needed[20] in view of eq 6, which derive from eq 5. The k_{dif} values were obtained from the Debye equation.[17]

$$1/k_q = (1/k_{dif}) + (\gamma/k_{ET}) \qquad (6a)$$

$$1/k_q\tau = 1/(k_{dif}\tau) + \gamma/(\tau k_{ET}) \qquad (6b)$$

$$\text{where } \gamma = (k_{-dif}/k_{dif})$$

The plot of $1/k_q\tau$ versus $1/k_{dif}$ is given in Figure 3 with hexane, methylcyclohexane, cyclohexane, and dodecane. This plot is useful since the slope is $1/\tau$ (note eq 6b). A value of τ = 8.1 ns is obtained.

Next we would like to obtain a value for k_q in the various solvents with benzene being of particular interest as the primary reaction solvent of our 6-alkylcyclohexenone study. Since τ is known, the intercept $(k_{ET}/\gamma\tau)^{-1}$ of our Figure 3 plot of eq 6b lets us obtain k_{ET}/γ, or $(k_{dif}k_{ET}/k_{-dif})$, with a value of 4×10^9 L·M^{-1}·s^{-1}.

If k_{ET}/γ along with the calculated k_{dif} values is used with eq 6a, we obtain the rates of quenching given in Table III.[18d]

Finally, the rates of quenching were used, in conjunction with the $k_q\tau$ values (i.e. the slopes) in Figure 2a, to afford the triplet lifetimes (i.e. the τ's) for the various compounds of interest.[21]

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(17) (a) The bimolecular rate constant for diffusion can be expressed as a function of solvent viscosity, η, and temperature, as $k_{dif} = 8RT/3000\eta$.[17b] For this study the viscosities were taken as those of the pure solvents at 20 °C.[17c] Use of alternative values of $k_{dif} = 8RT/2000\eta$ leads to rates of decay and reaction that are 1.5-fold. The choice of 3000 was predicted on the suggestion that 3000 is more appropriate where the solute molecule is large compared with the solvent size as commented by Birks,[20b] p 422, and Saltiel.[18b] (b) Debye, P. J. W. *Trans. Electrochem. Soc.* **1942**, *82*, 265. (c) Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, C. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, 1953.

(18) (a) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238. (b) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799–6808. (c) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1–90. (d) Either k_q or τ may be anomalous for benzene. However, if we assume k_{ET}[18b] and γ[18a] to be solvent independent then eq 6a affords a k_q that leads to an anomalous τ value. However, were we to assume that it is the benzene k_q which is unusual rather than the τ, using the 8.1-ns lifetime found in aliphatic solvents along with the Stern–Volmer slope for the parent enone in benzene, one obtains k_q as 1.4×10^9 L·M^{-1}·s^{-1}, which differs less than a factor of 2 from the 2.7×10^9 value derived with the reverse assumption.

(19) (a) Weller, A. *Discuss. Faraday Soc.* **1959**, *27*, 28; *Progr. React. Kinet.* **1961**, *1*, 192–193. (b) Reversible energy transfer is included in eq i. Thus, the experimental rate constant k_q can be expressed as in eq ii.[19c] Also, we have assumed that the decay of the encounter pair is low compared with dissociation and energy transfer and a τ term in the original denominator disappears in giving eq 5. For endothermic reversible transfer,

$$E \xrightarrow{h\nu} {}^3E^* + Q \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} {}^3(E^*{\cdot}Q) \underset{k_{-ET}}{\overset{k_{ET}}{\rightleftharpoons}} {}^3(E{\cdot}Q^*) \underset{k_{dif}}{\overset{k}{\rightleftharpoons}} E + {}^3Q^* \qquad (i)$$

$$k_q = \frac{k_{dif}}{1 + (k_{-dif}/k_{ET})\cdot[1 + (k_{-ET}/k_{-dif})]} \qquad (ii)$$

$k_{-ET} \ll k_{-dif}$, and eq ii reduces to eq 5. (c) Balzani, V.; Bolleta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2163.

(20) Equation 6 is readily derivable from the formulations of Wagner and Kochevar[18a] and Saltiel.[18b]

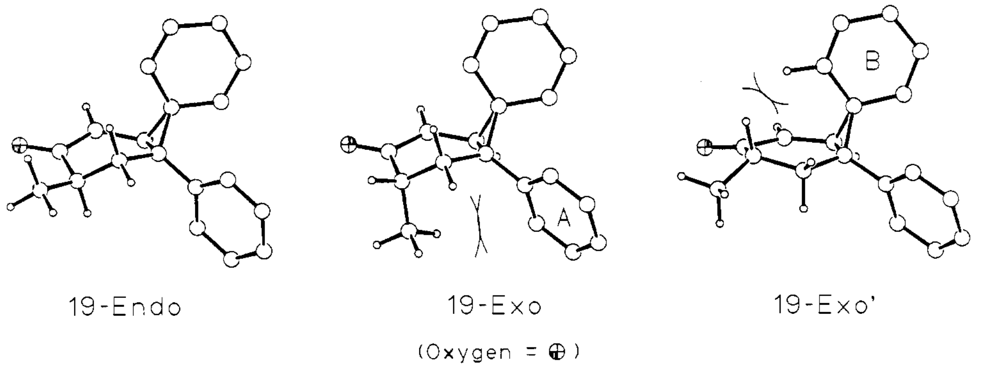


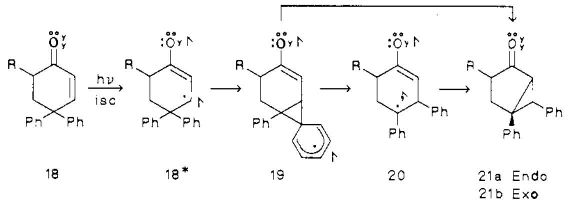
Figure 4. Ortep drawings of molecular mechanics minimized half-migrated triplet diradicals.

These, in turn, were used (i.e. $k_r = \phi/\tau$) to afford the rates of triplet reaction, which are presented in the Discussion Section.

It needs to be noted that the above treatment assumes that γ in eq 6 is constant. An alternative suggested by Saltiel[18b,c] is that γ is given by the solvent molarity. A treatment based on this assumption is presented in the Experimental Section and the results are included in Table III. It is seen that the resulting k_q's follow the same trend and each differ by less than a factor of 2.

Discussion

The Overall Reaction Mechanism and Stereochemistry. The rearrangement of the C-6 substituted 4,4-diphenylcyclohexenones proceeds in a fashion quite similar to that observed for the various 4,4-diarylcyclohexenones previously studied.[3] Throughout, there is a preference for formation of the trans configuration of the 5,6-substituents (bicyclic numbering; note **21** and **22**).[22] As in all these examples, in the present study the migrating phenyl group becomes trans. The overall mechanism is depicted in eq 7.



(7)

However, what was initially surprising was the kinetic preference for the C-3 endo stereoisomers **12a–16a** (i.e. **21a**) rather than the more stable exo isomer **12b–16b** (i.e. **21b**). Hence it is clear that the product-determining stage of the reaction must come early along the reaction hypersurface. The stereochemistry is understandable if one considers the species **19** in which the phenyl group is half-migrated.

Molecular mechanics[23] proved useful in comparing the half-migrated species **19-exo** and **19-endo**. The Ortep drawings of the MMP2 results are shown in Figure 4. There are two basic conformations possible for each diradical. **19-endo** is seen to have the C-6 substituent in a pseudo-equatorial conformation and away from the large phenyl groups. **19-exo** has the C-6 substituent pseudoaxial, 1,3-related to the phenyl group labeled "A". An alternative six-ring conformation **19-exo′** might be considered since this unfavorable interaction is then avoided. However, here there is exceptionally severe C-6 hydrogen–spiro phenyl (labeled B) interaction. These conclusions were confirmed by comparison of the MMP2 energies which are included in Table IV along with the photoproduct energies for R = methyl.

Table IV. Calculated Energies for the Methyl-Substituted Species

species	MMP2 steric energy (kcal/mol)
19-endo (R = Me)	14.21
19-exo (R = Me)	15.32
19-exo′ (R = Me)	17.41
endo-methyl photoproduct **21a**, R = Me (**15a**)	15.94
exo-methyl photoproduct **21b**, R = Me (**15b**)	14.71

Therefore, the "half-migrated" species **19-endo** leading to the C-3 endo bicyclic photoproduct (one of **12a–16a**) is seen to be preferred energetically over the "half-migrated" species **19-exo** which would afford the exo bicyclic photoproduct (one of **12b–16b**). The rate- and product-determining stage of the rearrangement must come near (actually prior to; note below) half-migration; and the rationale for formation of the less stable endo stereoisomer derives from lack of reversibility after the molecule reaches this point. This aspect is considered in more detail in connection with MO calculations described below.

Significance of the Reaction Quantum Yields. Intramolecular Singlet Energy Transfer. Reference to Table II permits a number of interesting conclusions. One is that the quantum yield is independent of whether the wavelength employed leads to selective absorption by the enone moiety as was the case for 366-nm photolyses or leads to a preferential absorption (ca. 60%) by the naphthyl group as in 313-nm photolyses.

This result is reasonable. First, singlet energy transfer from the excited naphthyl moiety to the enone chromophore is expected to be rapid and efficient. Second, especially facile intersystem crossing at the locus of the enone carbonyl group is anticipated. To the extent that these two expectations are valid, the triplets are "born" with excitation in the enone moiety and with an efficiency independent of which group is absorbing.

Singlet energy transfer is, indeed, exothermic since the S_1 energy of naphthyl is 90 kcal/mol[24] and that of the enone chromophore is 76 kcal/mol.[12] The facile singlet energy transfer is confirmed by the absence of naphthyl fluorescence in the naphthylbutyl and naphthylmethyl enones, **6** and **7**. Also, singlet energy transfer is known to occur over long distances;[25] here the greatest distance

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[21] (a) The modest size differences between the parent, naphthylmethyl, and naphthylbutyl enones are not expected to affect the actual k_{dif} values[21b] and ultimately the k_q value for each species. (b) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 1970.

[22] (a) This is equivalent to saying that the migrating aryl group becomes endo at C-6 of the bicyclic product. One exception[22b] is the photochemistry of 4,5,5-triphenylcyclohexenone where the migrating group attains the exo configuration as a result of steric interaction of an endo 4-phenyl group with any endo C-6 substituent. (b) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276–6289.

[23] (a) The MMP2[23b] program was used. (b) Allinger, N. L.; Flanagan, H. L. *J. Comput. Chem.* **1983**, *4*, 399.

[24] (a) The singlet energy of naphthalene[24b] and 1-methylnaphthalene[24c] was reported to be 92 and 90 kcal/mol, respectively. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 70. (c) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 5.

[25] There is considerable literature on long-range dipole–dipole singlet excitation transfer which is known to occur over distances up to 100 Å.[26] Energy transfer has also been studied in many bichromophoric systems.[27,28] That such energy transfer is rapid has precedent in our study[29] of singlet transfer in rod-like molecules from naphthyl to benzoyl groups ca. 7 Å apart; these rates were above 10^9 s^{-1}. Hammond et al.[30] studied the fluorescence from bichromophoric molecules in which a naphthyl group was attached to a benzophenone moiety by one, two, and three methylene chains. They concluded energy transfer from the excited naphthyl singlet to the benzophenone group proceeded with rates of 10^7–10^8 s^{-1}.

[26] (a) Forster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Ware, W. *J. Phys. Chem.* **1962**, *66*, 455. (c) Ware, W. *J. Am. Chem. Soc.* **1961**, *83*, 4374. (d) Bennet, R. G. *J. Chem. Phys.* **1964**, *41*, 3037.

[27] (a) Note ref 27a and 27b for reviews. (b) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383–389. (c) DeSchryver, F. C.; Boens, N. *Adv. Photochem.* **1977**, *10*, 359–465.

Table V. Triplet Lifetimes and Reaction Rates of Cyclohexenones[a]

enone	solvent	τ, ns	$(10^{-7})k_r$,[c] s^{-1}	$(10^{-8})k_d$, s^{-1}	ref
naphthylbutyl enone **6**	benzene	3.2 (2.1)	1.50 (2.3)	3.0 (4.5)	*b*
naphthylmethyl enone **7**[h]	benzene	0.30 (0.2)	1.46 (2.2)	32.3[d] (48)	*b*
parent enone **4**	benzene	3.9 (2.6)	1.11 (1.7)	2.47 (3.7)	3b
parent enone **4**	*n*-dodecane	8.3 (5.5)	0.36 (.54)	1.21 (1.8)	3e
parent enone **4**	aliphatic[e]	8.1 (5.4)	0.39 (.59)	1.19 (1.8)	*b*
p-cyanophenylphenyl enone			10.1[f] (15.1)		
	benzene	1.8 (1.2)	0.92[g] (1.4)	5.65 (8.5)	3d

[a] Values obtained from Stern–Volmer slopes and quenching rate constants from Table III. Parenthesized values result from using the alternative Debye formulation. Errors in rate constants are estimated from standard deviations of Stern–Volmer slopes to be ca. ±10%. [b] This study. [c] Total reaction rate of triplet enone. [d] Rate of normal decay of enone plus that of intramolecular triplet energy transfer to the naphthyl group. [e] Hexane, methylcyclohexane, cyclohexane, *n*-dodecane. [f] Rate of *p*-cyanophenyl migration. [g] Rate of phenyl migration. [h] The rates for the naphthylmethyl enone are for T_2.

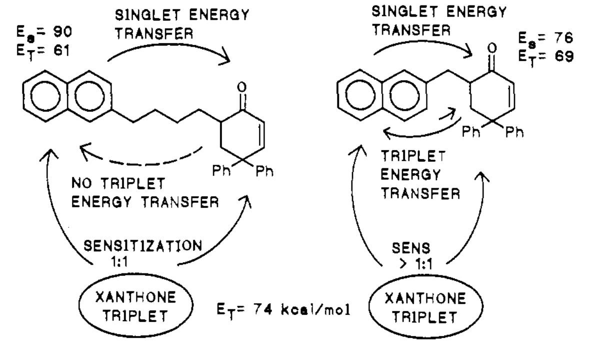
is ca. 7 Å with an extended butyl chain in **6**. Second, intersystem crossing is known to be especially rapid at the locus of carbonyl groups as a consequence of spin–orbit coupling.[31]

Intramolecular Triplet Energy Transfer Conclusions from the Quantum Yield Results. A second interesting conclusion deriving from the results in Table II deals with the different efficiencies observed for the naphthylbutyl versus the naphthylmethyl enones **6** and **7**, respectively. The quantum efficiency (0.048) for the naphthylbutyl enone **6** is within experimental error of that of the parent diphenyl enone **4** (0.043) and also within experimental error of the efficiency of the methyl and propyl derivatives (ϕ = 0.050 for **9** and ϕ = 0.047 for **10**).

From this we can conclude that in enone **6** no triplet quenching is occurring by intramolecular energy transfer to the naphthyl group despite its lower triplet energy (61 kcal/mol[13]) relative to the enone triplet variously estimated as 61–69 kcal/mol[33] and despite the known ability of naphthalene to quench the diphenylcyclohexenone triplet when utilized as an external energy acceptor.[3b] Apparently the separation between the enone and naphthyl chromophores due to the butyl chain linkage diminishes the short-range exchange mechanism responsible for triplet energy transfer[35] to such an extent that energy transfer does not compete with the reaction and decay processes of the enone.

In contrast, naphthylmethyl enone **7** had a markedly diminished quantum efficiency (0.0059) compared with all of the above, although as noted this quantum yield was independent of the chromophore irradiated. We conclude that in this case the less remote naphthyl group is effecting intramolecular quenching of the enone triplet moiety. However, evidence supports the reversibility of this quenching process.

Scheme II. Energy-Transfer Processes Occurring in the Naphthylalkyl Enones



It has been noted that in Figure 2a the Stern–Volmer intercept for the naphthylmethyl enone was 1.3 rather than the anticipated 1.0. This provides evidence for the existence of two triplets. The higher energy triplet T_2 corresponds to the enone moiety being locally excited while the lower energy triplet T_1 has the energy localized in the naphthyl group. Indeed, the extrapolated quantum yield for zero quencher concentration is 0.0045 which is 76% of the unquenched efficiency (0.0059). This corresponds to the quantum yield deriving from the short-lived T_2 alone; the Stern–Volmer slope at higher quencher concentrations derives from conditions where all of the longer lived T_1 triplet has been annihilated. Thus the residual 24% of the unquenched quantum yield (i.e. 0.24 × 0.0059 = 0.0014) must come from T_1 and uphill energy transfer from the naphthyl to the enone chromophore.[36]

Conclusions Bearing on the Nature of Intermolecular Sensiti-

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(28) (a) Schnepp, O.; Levy, M. *J. Am. Chem. Soc.* **1962**, *84*, 172–177. (b) Latt, S.; Cheung, H. T. *Ibid.* **1965**, *97*, 995–1003. (c) Breen, D. E.; Keller, R. A. *Ibid.* **1968**, *90*, 1935–1940. (d) Keller, R. A. *Ibid.* **1968**, *90*, 1940. (e) Keller, R. A.; Dolby, L. J. *Ibid.* **1969**, *91*, 1293–1299. (f) Rauh, R.; Evans, T. R.; Leermakers, P. A. *Ibid.* **1968**, *90*, 6897–6904. **1969**, *91*, 1868–1870. (g) Lamola, A. A. *Ibid.* **1969**, *91*, 4786. (h) Armein, W.; Schaffner, K. *Helv. Chim. Acta* **1975**, *58*, 397–415. (i) Stryer, L.; Haughland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 719–726. (j) Kuhn, H. *Mol. Cryst.* **1967**, *2*, 199–230.

(29) (a) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951. (b) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645.

(30) Lamola, A. A.; Leermakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322–2331.

(31) (a) Facile intersystem crossing in the enone moiety should follow as a consequence of spin–orbit coupling[31b] at the carbonyl group. The rate of intersystem crossing for naphthalene[31c] is 5 × 10^6 s^{-1} and that for conjugated ketones is on the order of 10^{11}–10^{12} s^{-1}.[31d] Thus, it seems likely that at time zero, when intersystem crossing to afford a triplet first occurs, it is the enone triplet chromophore that is engendered. This has parallel in our other studies.[3g,32] (b) El-Sayed, M. A. *J. Chem. Phys.* **1964**, *41*, 2462. (c) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14–19. (d) For benzophenone, a value of 10^{11} s^{-1} has been reported: Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500–2511. For acetophenone, a value of 10^{12} s^{-1} 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.

(32) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.

(33) The vertical triplet energy as determined spectroscopically has been reported as 69 kcal/mol.[12b] Recently, evidence in the form of a laser-detected transient was presented[34] for the presence of a 61–63 kcal/mol cyclohexenone triplet absorbing at 280 nm. More recently a ground-state twisted enone structure has been proposed for this transient.

(34) (a) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706–2707. (b) Chan, C. B.; Schuster, D. I. *Ibid.* **1982**, *104*, 2928–2929. (c) Pienta, N. J. *Ibid.* **1984**, *106*, 2704–2705.

(35) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850.

(36) (a) The lifetime of naphthalene in benzene is reported to be ca. 1 ms.[36b] Thus, the rate of energy transfer from the naphthyl triplet to the enone would only have to be on the order of 10^3 s^{-1} to compete with the normal naphthyl triplet decay. (b) Tsai, S. C.; Robinson, G. W. *J. Chem. Phys.* **1968**, *49*, 3184–3191. (c) With k_{ET} now known as 2.9 × 10^9 s^{-1}, we can consider whether the 8 kcal/mol unfavorable endothermic energy transfer from naphthyl to enone will actually permit the 0.0018 observed quantum efficiency of the thioxanthone-sensitized runs. The 8 kcal/mol corresponds to an unfavorable preequilibrium constant $k_{eq} = k_{ET}/k_{ET}$ of 1.4 × 10^{-6}. Of some interest first is the k_{-ET} value, the rate of endothermic energy transfer, for which we now solve as 4.1 × 10^3 s^{-1}. This signifies that the rate of population of the enone triplet is more than comparable with the rate of decay via the naphthyl moiety triplet.[36a] However, the effective rate of enone rearrangement starting with T_1 is of particular interest, since this will permit quantum yield assessment. Since $k_r(T_1) = k_{eq}k_r(\text{enone})$, we obtain $k_r(T_1)$ as 15 s^{-1} by using the value of 1.1 × 10^7 s^{-1} of 4,4-diphenylcyclohexenone itself. The quantum yield, $\phi = k_r(T_1)/(k_r(T_1) + k_{d(tol)})$, has as its upper limit 0.015 when we take the total rate of decay $k_{d(tol)}$ as 10^3 or the decay rate of an isolated naphthyl group. This compares with the observed efficiency of 0.0018 in thioxanthone sensitization. If we conclude further modes of decay (e.g., due to interaction between enone and naphthyl chromophores) we obtain $k_{d(extra)}$ = 7.3 × 10^3 s^{-1}. In any case, sufficient endothermic transfer occurs to account for the observed efficiency. Finally, in this case of the naphthylmethyl enone **7** whether thioxanthone transfers energy to the naphthyl group or to the enone moiety directly is moot, since a rapid preequilibrium is established. Further, observation of the same quantum yield with xanthone (74 kcal/mol) confirms this conclusion.

zation Derived from the Quantum Yield Results. A third conclusion deriving from the results in Table II is relevant to the nature of intermolecular energy transfer and sensitization in the present chemistry. Thus, the quantum efficiency of the naphthylbutyl enone **6** using a xanthone (74 kcal/mol[11a]) sensitizer is seen to be just half (ϕ = 0.023) that of the direct irradiations. Hence, capture of the sensitizer triplet by the nonreacting and lethal naphthyl group is about equally efficient compared with capture by the reactive diphenyl enone moiety.

This strongly suggests an intriguing interpretation of energy transfer and sensitization in such exothermic cases as the present. Thus, bumping of the xanthone triplet into the naphthyl and diphenyl enone ends of molecule **6**, with energy transfer, has about equal probability. This result is especially interesting in view of the known[37] preferential triplet energy transfer between species having π–π* and n–π* excited states. This means that if transfer after encounter had been rate-limiting, xanthone would have excited the naphthyl group more efficiently than the enone moiety.

The example of naphthylmethyl enone **7** is quite different. Here the quantum efficiency on sensitization is low (ϕ = 0.0017, only 29% of the direct quantum yield). If energy transfer to the enone end of the molecule again resulted from about half of the molecular encounters between sensitizer and acceptor **7**, one would have anticipated an efficiency of at least 0.0030. One interpretation of the low reaction efficiency is that in naphthylmethyl enone **7**, it is difficult for the sensitizer triplet to approach the enone moiety without also being near the naphthyl group as well. Moreover, in view of the uphill energy transfer from the naphthyl triplet to the enone discussed above, complete sensitization of the naphthyl moiety would account for the observed sensitized quantum yield (vide infra).

A final point concerns the efficiency (ϕ = 0.0018) of thioxanthone (E_T = 65 kcal/mol[11b]) sensitization of naphthylmethyl enone **7** rearrangement. Selective sensitization of the naphthyl moiety (E_T = 61 kcal/mol[13]) is expected on the basis of exothermicity. The efficiency here is expected to be the same as that observed from populating T_1 as discussed above in the quenching studies. That efficiency is 0.0014 and is thus experimentally acceptable.

A convenient summary of the various energy transfer processes occurring in naphthylalkyl enones **6** and **7** is presented in Scheme II.

Determination of Triplet Lifetimes and Reaction Rates. As noted at the outset, our objective was to obtain independent quenching rates rather than using rates of diffusion. The k_q values for cyclohexadiene quenching 4,4-diphenylcyclohexenone, as given in Table III, are seen to be lower than the rates of diffusion. However, as the viscosity of the solvent increases, the k_q's come within a factor of 2 of the rates of diffusion. This is as expected, if one looks at eq 5, since k_{dif} becomes smaller relative to k_{ET}.

Using the presently obtained values (note Table III) for k_q along with the Stern–Volmer slopes of Figure 2, we obtain triplet lifetimes and triplet reaction rates using the approach discussed earlier in the Results Section. These values are given in Table V. We include recalculated values for the parent diphenyl enone **4** and its *p*-cyano relative, since we now have an improved quenching rate.

It should be noted, nevertheless, that the rate of cyclohexadiene quenching we have obtained (e.g. 3×10^9 L·M^{-1}·s^{-1} in benzene) is close, although 2-fold less, than the value of 6×10^9 L·M^{-1}·s^{-1} commonly used[15] and the value used for diphenyl enone **4** in our most recent studies.[3g]

Assessment of the Rate of Intramolecular Energy Transfer. Reference to Table V reveals a considerably more rapid rate of triplet decay (i.e. k_d) for naphthylmethyl enone **7** than parent diphenyl enone **4** as well as naphthylbutyl enone **6**.

Let us focus attention on conditions where the quencher concentration is sufficient to deplete T_1 giving the T_2 portion of the Stern–Volmer plot in Figure 2. The slope there reflects normal enone vertical decay along with irreversible energy transfer to the naphthyl group. Hence we can assume that k_d for naphthylmethyl enone **7** is the sum of (i) the rate of decay characteristic of cyclohexenones without proximate naphthyl groups (as in parent enone **4** or naphthylbutyl enone **6**) and (ii) the rate of intramolecular energy transfer (i.e. k_{ET}) from the enone triplet moiety to the nearby naphthyl group. Simple subtraction (i.e. $k_{d(7)} - k_{d(6)}$) gives us the additional decay (k_{ET}) due to intramolecular triplet transfer. We obtain $k_{ET} = 2.9 \times 10^9$ s^{-1}.[36c]

A final point here is that the intramolecular energy transfer process is fast compared with conformational equilibration (ca. 10^7–10^8 s^{-1})[38] and thus the extended conformations considered above are justified.

Dissection of the Intermolecular Energy Transfer Processes. In the Results Section we report the value of k_{ET}/γ, where γ was defined as k_{-dif}/k_{dif}. With a value of γ in hand, one can better understand the nature of the energy transfer process depicted in eq 4a and 4b; γ has been assigned a value of 4 M·L^{-1} based on random walk theory.[18a] This leads to a value of 1.6×10^{10} s^{-1} for k_{ET}. Thus, in eq 4b, with k_{dif} being 10^{10} L·M^{-1}·s^{-1} for benzene,[17] k_{-dif} is 4×10^{10} s^{-1}. Thus, all three rate processes in eq 4b are of the same order of magnitude; and one can see that quenching is not controlled uniquely by either forward step, diffusion or energy transfer following each encounter.

One interesting approach is to use T_2 of naphthylmethyl enone **7** as a model to approximate an encounter pair involving an enone triplet and a naphthalene ground state. It is true that exact distance and relative orbital orientation may differ in **7** from an encounter pair; but the approximation seems worthwhile and the results are reasonable. This permits us to use the value k_{ET} obtained for the proximate enone and naphthyl moieties in **7** along with eq 6a and the value of γ to obtain rates of enone quenching by naphthalene in a variety of solvents. For benzene we obtain $k_q = 7 \times 10^8$ L·M^{-1}·s^{-1}. Similarly, for isopropyl alcohol we obtain $k_q = 6 \times 10^8$ L·M^{-1}·s^{-1}, which is very close to the value of 4×10^8 L·M^{-1}·s^{-1} reported by Schuster.[34a]

Comparison of Intramolecular versus Intermolecular Quenching. A significant finding is the ca. 88% intramolecular enone triplet quenching (vide supra) observed in the naphthylmethyl enone **7** contrasted with a ca. 7% effectiveness of energy transfer of encounter pairs in the intermolecular naphthalene–enone quenching process. This is seen in the comparison of 2.9×10^9 s^{-1} for k_{ET} (i.e. successful quenching) versus 4×10^{10} for k_{-dif} (i.e. failure to quench) by an encounter pair. We can take naphthylmethyl enone triplet **7*** as a model for an intermolecularly formed encounter pair, however one in which back diffusion is precluded; we see that back diffusion is a major factor in diminishing quenching efficiency.

The Nature of the Enone Triplet and Facility of Quenching. The rate of parent enone **4** triplet quenching by naphthalene is 6-fold slower than by cyclohexadiene as was recognized in our early study.[3b] Using this earlier work, together with the 3×10^9 L·M^{-1}·s^{-1} value for cyclohexadiene, we obtain k_q for naphthalene as 5×10^8 L·M^{-1}·s^{-1}, a value remarkably close to the 7×10^8 L·M^{-1}·s^{-1} rate derived above from eq 6a using the rate of intramolecular energy transfer found in naphthylmethyl enone **7**.

One point not yet considered is whether the slow quenching by naphthalene derives from a less exothermic quenching process than commonly assumed or, relatedly, from a twisted enone

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(37) (a) A preference for energy transfer from ^{3}(n–π*) to ^{3}(π–π*) over ^{3}(n–π*) to ^{3}(n–π*) has been described by several authors.[37b–d] Mirbach et al.[37b] report much slower rates of energy transfer for the ^{3}(n–π*) to ^{3}(n–π*) type due to localization of the excitation and poor overlap between donors and acceptors. (b) Mirbach, M. R.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471–474. (c) Saltiel et al.[18b] noted the localization of excitation in triplet acetone. (d) See also Wagner and Kochevar.[18a] (e) The possibility that T_1 and T_2 might be the n–π* and π–π* enone triplets has not been discussed. However, this is apparent from the absence of nonlinear Stern–Volmer behavior for all 4,4-diarylcyclohexenones thus far except for the special case of naphthylmethyl enone 7.

(38) (a) Winnik, M. *Chem. Rev.* **1981**, *81*, 491. (b) Nairn, J.; Braun, C. *J. Chem. Phys.* **1981**, *74*, 2441. (c) Nairn, J.; Braun, C.; Caluwe, P.; Szwarc, M. *Chem. Phys. Lett.* **1978**, *54*, 469. (d) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1978**, *100*, 7171. (e) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Ibid.* **1986**, *108*, 3618–3620. (f) Yang, N. C.; Neoh, S.; Naito, T.; Ng, L.-K.; Chernoff, D.; McDonald, D. *Ibid.* **1980**, *102*, 2806.

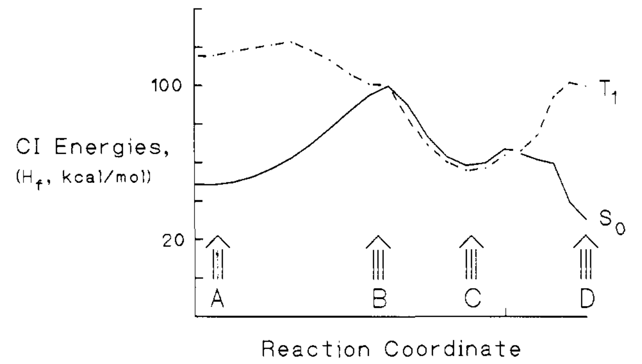

Figure 5. Singlet and triplet reaction hypersurfaces for 4,4-diphenylcyclohexenone. A corresponds to starting enone, B to the phenyl half-migrated species, C to the open diradical **20** (R = H), and D to bicyclic photoproduct 11.

triplet.[34] The latter would result in a low k_{ET} due to enone twisting being necessary for triplet generation. While such twisting seems likely to occur in view of a lowered α–β bond order in the excited state, MNDO–CI[39] geometry optimization on cyclohexenone itself (note Experimental Section for details) reveals a modest 45° twist with a ca. 3 kcal/mol stabilization.

Further, phosphorescence emission evidence[12b] suggests cyclohexenones to have triplet energies of ca. 69 kcal/mol. Triplet emission generally occurs from the 0th vibrational excited state level and thus provides the energy of the relaxed triplet.[40] This, too, suggests that energy lowering of the enone triplet by twisting is minimal.

Any enone triplet twisting would account for some energy of activation in the energy transfer process. The transition state and activation energy must reflect the exothermicity of the overall process. Hence one would anticipate cyclohexadiene to accept energy more rapidly than naphthalene.

MO Treatment of the Reaction. It seemed of interest to assess the nature of the reaction hypersurface. For this purpose MNDO–CI[39] was used. For points along the reaction coordinate, geometry was optimized for the ground state (i.e. S_0). For each point, the singlet and triplet energies were obtained with minimal configuration interaction of the SCF MO's. Figure 5 shows the surfaces obtained.

Several points are noteworthy. First, the vertical triplet enone A is predicted to have a small energy barrier (ca. 8 kcal/mol) in agreement with our earlier experimental findings of 10 kcal/mol.[3e] Second, the phenyl bridged diradical B (**19**, R = H) appears to be at most a shallow minimum, and at this point the ground state and triplet surfaces first meet; it is possible that with more extensive configuration interaction the minimum will deepen. Third, the open diradical C (**20**, R = H) resulting from completion of migration appears to be formed in preference to a process in which three-ring closure occurs concerted with migration. This possibility has already been considered,[3b] and the observed 6-endo phenyl preference is understandable on the basis of noninterference with the nonmigrating phenyl group. The latter is conformationally fixed due to odd-electron delocalization of one center of the diradical, and thus it is especially susceptible to steric effects. Radiationless decay with intersystem crossing to the ground state seems most likely to occur in the open diradical C (**20**, R = H).

Conclusion. The present study is part of our continuing efforts to focus on molecular and electronic details of photochemical reactions of special generality and interest. Again, we find that excited state rearrangements are subject to the same types of stereochemical and mechanistic control seen in ground state processes.

Experimental Section[41]

4,4-Diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone (6).[42] To a refluxing solution of 24.6 mmol of isopropylmagnesium bromide[41] in 20.0 mL of THF was added dropwise a solution of 6.60 g (20.0 mmol) of 4,4-diphenylcyclohexenone cyclohexylimine[5] in 14.0 mL of THF. The orange solution was refluxed for 1 h and cooled to room temperature, and a solution of 5.30 g (10.0 mmol) of 4-(2-naphthyl)-1-bromobutane[43] in 6.0 mL of THF was added. The dark solution was stirred at room temperature for 1 h, slowly quenched with 20 mL of 5% hydrochloric acid, and stirred overnight. Neutral workup[41] with methylene chloride afforded 9.80 g of a dark oil, which was chromatographed on a 5 × 75 cm silica gel column: fraction 1, hexane, 500 mL, nil; fraction 2, hexane, 1500 mL, 1.90 g of starting bromide; fraction 3, 5% ether in hexane, 1000 mL, nil; fraction 4, 10% ether in hexane, 750 mL, 2.00 g of alkylated enone product as a foam; fraction 5, 20% ether in hexane, 300 mL, 2.00 g of starting enone. The product was recrystallized from 95% ethanol to give 1.70 g (20%) of 4,4-diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone, mp 76–77 °C.

The spectral data were the following: IR (neat) 3048, 3024, 2925, 2848, 1680 (C=O), 1604, 1498, 1453, 1390, 1195, 825, 760, 710 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.7–7.9 (m, 3 H, arom), 7.1–7.6 (m, 15 H, arom and =CH), 6.19 (d, 1 H, J = 10 Hz, =CH), 2.6–2.8 (m, 3 H, aliph), 2.2–2.5 (m, 2 H, aliph), 1.9–2.1 (m, 1 H, aliph), 1.5–1.8 (m, 2 H, aliph), 1.3–1.5 (m, 3 H, aliph); MS, m/e 430.2297 (calcd for $C_{32}H_{30}O$, m/e 430.2297).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 88.99; H, 7.11.

Exploratory Direct Photolysis of 4,4-Diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone (6). A solution of 100 mg (0.23 mmol) of 4,4-diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone in 150 mL of photograde benzene was irradiated under nitrogen[41,44] with a 450-W Hanovia medium pressure mercury lamp through a sodium metavanadate filter solution[41] for 3.5 h. The photolysate was concentrated in vacuo to afford 100 mg of a light yellow oil which was shown by ^{1}H NMR to be free of starting enone. The photomixture was separated on a 20 × 20 cm preparative thick-layer silica gel plate, eluting with 10% ether in pentane. The fastest moving band gave 32 mg (32%) of *exo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a white solid, mp 87–90 °C. Band 2 contained 57 mg (57%) of *endo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a foam.

The spectral data for *exo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (CHCl$_3$) 3060,

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[39] (a) QCPE Program No. 455, Quantum Chemistry Program Exchange, Indiana University. Stewart, J. J. P.; Seiler, F. J. *QCPE Bull.* **1985**, *5*, 133–144. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4912.

[40] (a) Note, for example, the phosphorescence emission spectrum of biphenyl.[40b] (b) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820–2825.

[41] Melting points were determined by using 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) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by a hand-held UV lamp. Preparative thick-layerchromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was done by using a liquid chromatograph with an LDC 254-nm detector and LDC 5000 psi minipump. Analyses were done on a 0.55 × 25 cm polished stainless steel column packed with 3–7 μm porous silica beads. All reactions were run under dry nitrogen, and all solutions were purged with deoxygenated nitrogen[44] for 1 h prior to and during photolysis unless otherwise stated. Exploratory photolyses were done by using an Hanovia 450-W medium-pressure mercury lamp immersion apparatus fitted with a Pyrex filter sleeve and cooled with a recirculating filter solution. The filter solution employed was 0.01 M sodium metavanadate in 0.1 M sodium hydroxide; transmission, 0% below 340 nm, 90% above 350 nm. Anhydrous magnesium sulfate or sodium sulfate was used as drying agent. Neutral workup refers to diluting with the appropriate solvent, washing with water and brine, drying, filtering, and concentrating in vacuo. Hexane used in HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine, dried over anhydrous calcium hydride, passed through alumina, and distilled from calcium hydride. Photograde cyclohexane, methylcyclohexane, and *n*-dodecane were prepared in a similar fashion. Benzene used for photolysis was purified by washing with saturated aqueous potassium permanganate and concentrated sulfuric acid, water, sulfuric acid until no discoloration, saturated aqueous sodium bicarbonate, and brine, followed by drying over anhydrous calcium chloride, and then reflux and distillation from calcium hydride. Ethyl acetate used in HPLC was distilled from phosphorous pentoxide. Tetrahydrofuran (THF) was purified by storage over potassium hydroxide, followed by successive distillation under nitrogen from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. The isopropylmagnesium bromide solutions were freshly prepared by the addition of 1 equiv of 2-bromopropane to Mg turnings stirred in THF at room temperature. Solutions of lithium diisopropylamide were prepared by adding 1 equiv of 1.5 M *n*-butyllithium in hexane to diisopropylamine in ether at −78 °C.

[42] The general method of Stork and Dowd[4] as applied by Zimmerman, Albrecht, and Haire[5] was used.

[43] Studt, P. *Ann. Chem.* **1965**, *685*, 49–55.

[44] Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

3014, 2936, 2860, 1713 (C=O), 1603, 1498, 1448, 821, 765, 752, 745, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 HMz) δ 7.6–7.8 (m, 3 H, arom), 7.1–7.5 (m, 14 H, arom), 3.11 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.7–2.9 (m, 4 H, α-ketocyclopropyl and aliph), 2.00 (dd, 1 H, J = 13, 9 Hz, aliph), 1.6–1.8 (m, 1 H, aliph), 1.4–1.6 (m, 2 H, aliph), 1.0–1.3 (m, 4 H, aliph); MS, *m/e* 430.2298 (calcd for $C_{32}H_{30}O$, *m/e* 430.2297).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.08; H, 7.04.

The spectral data for *endo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (neat) 3058, 3028, 2933, 2858, 1716 (C=O), 1602, 1498, 1448, 1322, 1204, 1160, 1028, 815, 755, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.6–7.8 (m, 3 H, arom), 7.1–7.5 (m, 14 H, arom), 3.03 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.80 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.3–2.7 (m, 5 H, aliph), 2.02 (dd, 1 H, J = 13, 5 Hz, aliph), 1.2–1.5 (m, 2 H, aliph), 0.9–1.2 (m, 3 H, aliph); MS, *m/e* 430.2299 (calcd for $C_{32}H_{30}O$, *m/e* 430.2297).

Anal. Calcd for $C_{32}O_{30}O$: C, 89.26; H, 7.02. Found: C, 88.99; H, 7.36.

exo-3-(4-(2-Naphthyl)butyl)-_trans_-5,6-diphenylbicyclo[3.1.0]hexan-2-one (12b).[42] To a refluxing solution of 12.3 mmol of isopropylmagnesium bromide[41] in 10 mL of THF was added dropwise a solution of 3.30 g (10.0 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one cyclohexylimine[5] in 7.0 mL of THF. The solution was refluxed for 1.5 h, cooled to 0 °C, and a solution of 2.65 g (10.0 mmol) of 4-(2-naphthyl)-1-bromobutane[43] in 3.0 mL of dry THF was added. The mixture was stirred for 2 h while warming to room temperature, slowly quenched with 10 mL of 5% hydrochloric acid, and stirred overnight. Neutral workup[41] with methylene chloride afforded 5.80 g of a dark oil that was chromatographed on a 2.5 × 20 cm silica gel column: fraction 1, hexane, 500 mL, nil; fraction 2, 5% ether in hexane, 200 mL, 1.80 g of starting bromide; fraction 3, 5% ether in hexane, 200 mL, 1.30 g of alkylated bicyclo ketone product as a foam; fraction 4, 5% ether in hexane, 300 mL, 0.90 g of starting ketone. The product was recrystallized from 95% ethanol to afford 1.2 g (28%) of *exo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as white crystals, mp 90–92 °C. The spectral data were identical with the data from the minor product obtained via photolysis of 4,4-diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone.

Epimerization of _endo_-3-(4-(2-Naphthyl)butyl)-_trans_-5,6-diphenylbicyclo[3.1.0]hexan-2-one (12a). A mixture of 40.0 mg (0.093 mmol) of *endo*-3-((2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 50.0 mg (0.47 mmol) of sodium carbonate in 30.0 mL of 5:1 THF–water was refluxed for 5 days. Neutral workup[41] with ether afforded 48 mg of a yellow oil which was shown by ^{1}H NMR to be >95% of the *exo*-3-(4-(2-naphthyl)butyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

4,4-Diphenyl-6-((2-naphthyl)methyl)cyclohex-2-enone (7).[42] To a refluxing solution of 24.6 mmol of isopropylmagnesium bromide[41] in 20.0 mL of dry THF was added dropwise a solution of 6.60 g (20.0 mmol) of 4,4-diphenylcyclohexenone cyclohexylimine[5] in 14.0 mL of dry THF. The solution was refluxed for 1.5 h and cooled to room temperature, and a solution of 4.43 g (10.0 mmol) of 2-(bromomethyl)naphthalene in 6.0 mL of dry THF was added. The mixture was stirred at room temperature for 1 h, slowly quenched with 20 mL of 5% hydrochloric acid, and stirred for 1 h. Neutral workup[41] with methylene chloride afforded 8.85 g of a dark oil, which was chromatographed on a 6 × 40 cm silica gel column eluted with 5% ether in hexane: fraction 1, 3000 mL, nil; fraction 2, 1000 mL, 0.40 g of starting bromide; fraction 3, 500 mL, nil; fraction 4, 2500 mL, 2.86 g of alkylated enone product as a foam; fraction 5, 2000 mL, 1.87 g of starting enone. The product was recrystallized from 95% ethanol to give 2.43 g (31%) of 4,4-diphenyl-6-((2-naphthyl)methyl)cyclohex-2-enone, mp 116–117 °C.

The spectral data were the following: IR ($CHCl_3$) 3061, 3028, 3010, 2925, 1678 (C=O), 1600, 1493, 1447, 1235, 1190, 816, 781, 758, 746, 736, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.7–7.9 (m, 3 H, arom), 7.0–7.5 (m, 15 H, arom and =CH), 6.26 (d, 1 H, J = 10 Hz, =CH), 3.62 (dd, 1 H, J = 14, 3.5 Hz, Ar-CH-*H*), 2.5–2.9 (m, 3 H, aliph), 2.29 (dd, 1 H, J = 14, 13 Hz, Ar-CH-*H*); MS, *m/e* 388.1837 (calcd for $C_{29}H_{24}O$, *m/e* 388.1827).

Anal. Calcd for $C_{29}H_{24}O$: C, 89.66; H, 6.23. Found: C, 89.77; H, 5.94.

Exploratory Direct Photolysis of 4,4-Diphenyl-6-((2-naphthyl)methyl)hex-2-enone (7). A solution of 200 mg (0.52 mmol) of 4,4-diphenyl-6-((2-naphthyl)methyl)cyclohex-2-enone in 250 mL of photograde benzene was irradiated under nitrogen[41,44] with a 450-W Hanovia medium-pressure mercury lamp through a sodium metavanadate filter solution[41] for 30 h. The photolysate was concentrated in vacuo to afford 200 mg of a light yellow oil that was shown by ^{1}H NMR to be free of starting enone. The photomixture was chromatographed on a 1 × 65 cm silica gel column: fraction 1, 2% ether in hexane, 450 mL, nil; fraction 2, 2% ether in hexane, 300 mL, 66 mg (33%) of *exo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a foam; fraction 3, 4% ether in hexane, 100 mL, nil; fraction 4, 4% ether in hexane, 200 mL, 100 mg (50%) of *endo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a white solid, mp 136–137 °C.

The spectral data for *exo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 3060, 3028, 3012, 1717 (C=O), 1603, 1496, 1448, 1320, 1180, 920, 826, 810, 755, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.6–7.8 (m, 3 H, arom), 7.1–7.5 (m, 13 H, arom), 6.99 (br d, 1 H, J = 10 Hz, arom), 3.17 (dd, 1 H, J = 14, 5 Hz, ArCH-H), 3.13 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.77 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.35–2.65 (m, 2 H, *exo*-cyclopentyl and ArCH-H), 2.14 (dd, 1 H, J = 13, 9 Hz, *endo*-cyclopentyl), 1.5–1.6 (m, 1 H, α-ketocyclopentyl); MS, *m/e* 388.1825 (calcd for $C_{29}H_{24}O$, *m/e* 388.1827).

Anal. Calcd for $C_{29}H_{24}O$: C, 89.66; H, 6.23. Found: C, 89.30; H, 6.51.

The spectral data for *endo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 3062, 3030, 3013, 1716 (C=O), 1603, 1498, 1448, 1160, 1013, 821, 754, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.1–7.8 (m, 16 H, arom), 6.94 (br d, 1 H, J = 8 Hz, arom), 3.10 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.88 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.7–2.9 (m, 1 H, α-ketocyclopentyl), 2.73 (dd, 1 H, J = 14, 4 Hz, Ar-CH-H), 2.41 (t, 1 H, J = 13 Hz, *exo*-cyclopentyl), 2.15 (dd, 1 H, J = 13, 5 Hz, *endo*-cyclopentyl), 0.87 (dd, 1 H, J = 14, 12 Hz, ArCH-H); MS, *m/e* 388.1829 (calcd for $C_{29}H_{24}O$, *m/e* 388.1827).

Anal. Calcd for $C_{29}H_{24}O$: C, 89.66; H, 6.23. Found: C, 89.37; H, 6.55.

exo-3-((2-Naphthyl)methyl)-_trans_-5,6-diphenylbicyclo[3.1.0]hexan-2-one (13b). To a −78 °C solution of 3.40 mmol of lithium diisopropyl amide[41] in 2.0 mL of dry ether was added dropwise a solution of 840 mg (3.40 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one[3a] in 6.0 mL of ether. After the solution was stirred for 20 min at −78 °C, 748 mg (3.40 mmol) of 2-(bromomethyl)naphthalene in 3.0 mL of dry ether was added. The mixture was stirred at −78 °C for 1 h and then at room temperature for 4 h before being quenched with water. Neutral workup[41] with ether afforded 1.45 g of a yellow oil, which was chromatographed on a 4 × 40 cm silica gel column: fraction 1, 3% ether in hexane, 1000 mL, nil; fraction 2, 5% ether in hexane, 750 mL, 187 mg of starting bromide; fraction 3, 5% ether in hexane, 1000 mL, nil; fraction 4, 10% ether in hexane, 1000 mL, nil; fraction 5, 10% ether in hexane, 1000 mL, 930 mg (71%) of *exo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a foam. The spectral data were identical with the data from the minor product obtained via the photolysis of 4,4-diphenyl-6-((2-naphthyl)methyl)cyclohex-2-enone.

Epimerization of _endo_-3-((2-Naphthyl)methyl)-_trans_-5,6-diphenylbicyclo[3.1.0]hexan-2-one (13a). A mixture of 50.0 mg (0.13 mmol) of *endo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 50.0 mg (0.47 mmol) of sodium carbonate in 30.0 mL of 5:1 THF–water was refluxed for 5 days. Neutral workup[41] with ether afforded 48 mg of a yellow oil that was shown by ^{1}H NMR to be >95% of *exo*-3-((2-naphthyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Exploratory Sensitized Photolyses of 4,4-Diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone (6) and 4,4-Diphenyl-6-(4-(2-naphthyl)methyl)cyclohex-2-enone (7). Successive photolyses were performed to compare conversions of the naphthylalkyl enones when subjected to xanthone or thioxanthone sensitization. Thus, solutions of enone and sensitizer in 150 mL of photograde benzene were irradiated under nitrogen[41,44] with a 450-W Hanovia medium-pressure mercury lamp through a sodium metavanadate filter solution[41] for 1 h. The photolysates were concentrated and assayed by ^{1}H NMR confirming the presence of the epimeric bicyclic photoproducts. The results were as follows: Run 1, solution of 87.0 mg (0.20 mmol, 0.0013 M) of 4,4-diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone and 1.0 g (5.5 mmol, 0.037 M) of xanthone, 100% conversion; Run 2, solution of 78.0 mg (0.20 mmol, 0.0013 M) of 4,4-diphenyl-6-(4-(2-naphthyl)methyl)cyclohex-2-enone and 1.0 g (5.5 mmol, 0.037 M) of xanthone, 100% conversion; Run 3, solution of 87.0 mg (0.20 mmol, 0.0013 M) of 4,4-diphenyl-6-(4-(2-naphthyl)butyl)cyclohex-2-enone and 1.0 g (4.7 mmol, 0.031 M) of thioxanthone, 15% conversion; Run 4, solution of 78.0 mg (0.20 mmol, 0.0013 M) of 4,4-diphenyl-6-(4-(2-naphthyl)methyl)cyclohex-2-enone and 1.0 g (4.7 mmol, 0.031 M) of thioxanthone, 62% conversion.

4,4-Diphenyl-6-((4-biphenylyl)methyl)cyclohex-2-enone (8).[42] To a refluxing solution of 13.0 mmol of isopropylmagnesium bromide[41] in 10.0 mL of THF was added dropwise a solution of 3.30 g (10.0 mmol) of 4,4-diphenylcyclohexenone cyclohexylimine[5] in 7.0 mL of THF. The solution was refluxed for 1 h and cooled to room temperature before 2.03 g (10.0 mmol) of 4-(chloromethyl)biphenyl in 3.0 mL of THF was added.

The mixture was stirred at room temperature for 45 min and refluxed for 2.5 h. Upon cooling the mixture was quenched with 10.0 mL of 10% hydrochloric acid and refluxed for 1 h. Neutral workup[41] with ether afforded 3.25 g of an orange oil that was chromatographed on a 5 × 60 cm silica gel column: fraction 1, 2% ether in hexane, 1500 mL, nil; fraction 2, 5% ether in hexane, 2000 mL, nil; fraction 3; 5% ether in hexane, 1000 mL, 0.40 g of starting chloride; fraction 4, 10% ether in hexane, 1000 mL, nil; fraction 5, 10% ether in hexane, 750 mL, 1.80 g of alkylated product as a white solid; fraction 6, 10% ether in hexane, 750 mL, 0.53 g of starting enone. The product was recrystallized from hexane to afford 1.70 g (41%) of 4,4-diphenyl-6-((4-biphenylyl)methyl)cyclohex-2-enone as white crystals, mp 113–115 °C.

The spectral data were the following: IR ($CHCl_3$) 3064, 3030, 3013, 2930, 1683 (C=O), 1600, 1491, 1449, 1389, 1233, 1188, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.0–7.7 (m, 20 H, arom and =CH), 6.25 (d, 1 H, J = 10 Hz, =CH), 3.47 (dd, 1 H, J = 14, 4 Hz, ArCH-H), 2.45–2.85 (m, 3 H, aliph), 2.29 (t, 1 H, J = 14 Hz, ArCH-H); MS, *m/e* 414.1993 (calcd for $C_{31}H_{26}O$, *m/e* 414.1993).

Anal. Calcd for $C_{31}H_{26}O$: C, 89.82; H, 6.32. Found: C, 89.60; H, 6.59.

Exploratory Direct Photolysis of 4,4-Diphenyl-6-((4-biphenylyl)methyl)cyclohex-2-enone (8). A solution of 200 mg (0.48 mmol) of 4,4-diphenyl-6-((4-biphenylyl)methyl)cyclohex-2-enone in 150 mL of photograde benzene was irradiated under nitrogen[41,44] with a 450-W Hanovia medium-pressure mercury lamp through a sodium metavanadate filter solution[41] for 6 h. The photolysate was concentrated in vacuo to afford 200 mg of a light yellow oil that was shown by ^1H NMR to be free of starting enone. The photomixture was chromatographed on a 3 × 35 cm silica gel column, eluted with 5% ether in hexane: fraction 1, 500 mL, nil; fraction 2, 325 mL, 80 mg (40%) of *exo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a foam; fraction 3, 75 mL, nil; fraction 4, 450 mL, 115 mg (58%) of *endo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a foam. The minor exo isomer was crystallized by vapor diffusion of hexane into toluene to afford crystals that were suitable for X-ray crystallography, mp 131–132 °C.

The spectral data for *exo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 3063, 3030, 3011, 2930, 1714 (C=O), 1496, 1488, 1447, 1410, 1318, 1178, 1075, 1009, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.2–7.6 (m, 17 H, arom), 6.99 (d, 2 H, J = 7.5 Hz, arom), 3.15 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 3.04 (dd, 1 H, J = 14, 5 Hz, ArCH-H), 2.75 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.4–2.55 (m, 2 H, *exo*-cyclopentyl and ArCH-H), 2.13 (dd, 1 H, J = 13, 9 Hz, *endo*-cyclopentyl), 1.4–1.6 (m, 1 H, α-ketocyclopentyl); MS, *m/e* 414.1994 (calcd for $C_{31}H_{26}O$, *m/e* 414.1984).

Anal. Calcd for $C_{31}H_{26}O$: C, 89.82; H, 6.32. Found: C, 89.83; H, 6.38.

The spectral data for *endo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 3060, 3028, 2955, 2930, 1721 (C=O), 1604, 1494, 1487, 1446, 1207, 1158, 1079, 1009, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.2–7.6 (m, 17 H, arom), 6.83 (d, 2 H, J = 7.5 Hz, arom), 3.10 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.87 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.7–2.9 (m, 1 H, α-ketocyclopentyl), 2.59 (dd, 1 H, J = 14, 4 Hz, ArCH-H), 2.46 (t, 1 H, J = 13 Hz, *exo*-cyclopentyl), 2.15 (dd, 1 H, J = 13, 5 Hz, *endo*-cyclopentyl), 0.71 (dd, 1 H, J = 14, 12 Hz, ArCH-H); MS, *m/e* 414.1989 (calcd for $C_{31}H_{26}O$, *m/e* 414.1984).

Anal. Calcd for $C_{31}H_{26}O$: C, 89.82; H, 6.32. Found: C, 89.45; H, 6.14.

***exo*-3-((4-Biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (14b).**[42] To a refluxing solution of 2.40 mmol of isopropylmagnesium bromide[41] in 5.0 mL of THF was added dropwise a solution of 0.656 g (2.00 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one cyclohexylimine[5] in 5.0 mL of THF. The dark solution was refluxed for 1 h and cooled to room temperature before a solution of 0.492 (2.00 mmol) of 4-(bromomethyl)biphenyl in 3.0 mL of THF was added. The mixture was stirred for 30 min, refluxed for 30 min, cooled, quenched with 20 mL of 5% hydrochloric acid, and stirred overnight. Neutral workup[41] with methylene chloride afforded 0.59 g of an orange semisolid that was chromatographed on a 3 × 35 cm silica gel column: fraction 1, 2% ether in hexane, 600 mL, nil; fraction 2, 4% ether in hexane, 400 mL, 183 mg of recovered bromide; fraction 3, 5% ether in hexane, 250 mL, 100 mg (12%) of product alkylated bicyclo ketone as a foam; fraction 4, 5% ether in hexane, 100 mL, 45 mg of a mixture of product and starting enone; fraction 5, 5% ether in hexane, 300 mL, 52 mg of starting enone. The spectral data of the product *exo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were identical with the data from the minor product obtained via the photolysis of 4,4-diphenyl-6-((4-biphenylyl)methyl)cyclohex-2-enone.

Table VI. Summary of Crystal Data and Intensity Collection Parameters for *exo*-3-((4-Biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one

molecular formula	$C_{31}H_{26}O$
molecular weight	414.55
cell parameters	
a (Å)	7.597 (4)
b (Å)	10.029 (4)
c (Å)	16.137 (7)
α (deg)	99.41 (3)
β (deg)	102.85 (4)
γ (deg)	97.55 (4)
space group	$P_{\bar{1}}$
molecules per cell (Z)	2
dimensions (mm)	0.60 × 0.25 × 0.10
d(calcd) (g/cm^3)	1.18
μ(calcd), (cm^{-1})	0.6
temp (°C)	25
scan mode	ω
scan speed (deg/min)	variable (1.50–29.3)
scan range (deg above $K_{\alpha 1}$/deg below $K_{\alpha 2}$)	0.6/0.6
two θ limits (deg)	4.0–45.8
standard reflcns	(−1,0,−2); (0,2,−2); (−1,−1,4)
freq of standards	3 per 100
no. of reflcns measured	3481
no. of unique reflcns	3197
cutoff for obsd data	$F > 3\sigma(F)$
no. of obsd reflcns	1730
anisotropic convergence (%)	$R_1(F) = 0.109$ $R_w(F) = 0.091$
goodness of fit	1.97

Epimerization of *endo*-3-((4-Biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (14a). A mixture of 50.0 mg (0.12 mmol) of *endo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 50.0 mg (0.47 mmol) of sodium carbonate in 10.0 mL of 1:1 dioxane–water was refluxed for 5 days. Neutral workup[41] with ether afforded 51 mg of a clear oil that was shown by ^1H NMR to be >95% of the *exo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Single Crystal X-ray Structure of *exo*-3-((4-Biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (14b). Crystals of *exo*-3-((4-biphenylyl)methyl)-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were prepared by vapor diffusion of hexane into toluene. X-ray data were collected with Mo Kα radiation on a Nicolet (Syntex) P-1 diffractometer from a parallelpiped shaped crystal of dimensions 0.60 × 0.25 × 0.10 mm. Unit cell parameters were obtained by least-squares refinement of 23 reflections ($5.3 < 2\theta < 23.7$). Data were collected in the (*hkl*) range (0,−11,−18) to (9,11,18) with 3 reflections monitored every 100. A total of 3197 unique data were collected, with 1730 of $F > 3\sigma(F)$. Lorentz and polarization correction were applied and the structure solved under $P_{\bar{1}}$ symmetry by direct methods with SHELXS86.[45] Hydrogen atoms were located from difference Fourier syntheses and full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement of 356 parameters converged to $R_1(F) = 0.109$ and $R_w(F) = 0.091$. Results are summarized in Table VI. Tables of atomic coordinates, bond angles, bond distances, and isotropic and anisotropic thermal parameters are given in the Supplemental Material.

4,4-Diphenyl-6-methylcyclohex-2-enone (9).[42] To a refluxing solution of 12.3 mmol of isopropylmagnesium bromide[41] in 20.0 mL of THF was added dropwise a solution of 3.30 g (10.0 mmol) of 4,4-diphenylcyclohexenone cyclohexylimine[5a] in 14.0 mL of THF. The orange solution was refluxed for 1 h and cooled to room temperature before 1.70 g (12.0 mmol) of iodomethane was added. The solution was stirred at room temperature for 30 min, slowly quenched with 10 mL of 5% hydrochloric acid, and stirred for 1 h. Neutral workup[41] with methylene chloride afforded 2.45 g of a dark yellow oil that was chromatographed on a 3 × 40 cm silica gel column, eluted with 5% ether in hexane: fraction 1, 1500 mL, nil; fraction 2, 200 mL, 1.27 g of product alkylated enone as a white solid, mp 97–101 °C; fraction 3, 1000 mL, 0.63 g of starting

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

(46) Gurney, R. W. *Ionic Processes in Solution*; McGraw-Hill: New York, 1953; pp 179–180.

enone. The product was recrystallized from ether in hexane to give 1.05 g (40%) of 4,4-diphenyl-6-methylcyclohex-2-enone, mp 103–105 °C.

The spectral data were the following: IR (neat) 3063, 3029, 3012, 2968, 2934, 2874, 1680 (C═O), 1600, 1493, 1445, 1376, 1229, 1189, 1062, 1029, 885, 810, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.1–7.4 (m, 11 H, arom and ═CH), 6.20 (d, 1 H, J = 10 Hz, ═CH), 2.4–2.7 (m, 3 H, aliph), 1.15 (d, 3 H, J = 5 Hz, methyl); MS, m/e 262.1359 (calcd for $C_{19}H_{18}O$, m/e 262.1358).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.53; H, 6.99.

Exploratory Direct Photolysis of 4,4-Diphenyl-6-methylcyclohex-2-enone (9). A solution of 400 mg (1.53 mmol) of 4,4-diphenyl-6-methylcyclohex-2-enone in 150 mL of photograde benzene was irradiated under nitrogen[41,44] with a 450-W Hanovia medium-pressure mercury lamp through a sodium metavanadate filter solution[41] for 4.5 h. The photolysate was concentrated in vacuo to afford 404 mg of a light yellow oil that was shown by ^{1}H NMR to be free of starting enone. This photomixture was chromatographed on a 2.5 × 30 cm silica gel column: fraction 1, 2% ether in pentane, 800 mL, nil; fraction 2, 3% ether in pentane, 150 mL, 80 mg (20%) of *exo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a clear oil; fraction 3, 4% ether in pentane, 500 mL, 300 mg (75%) of *endo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a clear oil.

The spectral data for *exo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (neat) 3060, 3030, 2965, 2930, 2870, 1717 (C═O), 1600, 1495, 1445, 1320, 1175, 1030, 825, 765, 730, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.25–7.45 (m, 10 H, arom), 3.13 (d, 1 H, J = 10 Hz, benzyl cyclopropyl), 2.70 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.67 (dd, 1 H, J = 13, 8 Hz, *exo*-cyclopentyl), 2.02 (dd, 1 H, J = 13, 9 Hz, *endo*-cyclopentyl), 1.05–1.25 (m, 1 H, α-ketocyclopentyl), 0.92 (d, 3 H, J = 7 Hz, methyl); MS, m/e 262.1362 (calcd for $C_{19}H_{18}O$, m/e 262.1358).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.67; H, 6.89.

The spectral data for *endo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (neat) 3060, 3030, 2970, 2935, 1720 (C═O), 1600, 1495, 1445, 1320, 1200, 1160, 1025, 920, 825, 765, 730, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.25–7.40 (m, 10 H, arom), 3.04 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.80 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.70 (t, 1 H, J = 13 Hz, *exo*-cyclopentyl), 2.4–2.6 (m, 1 H, α-ketocyclopentyl), 1.98 (dd, 1 H, J = 13, 5 Hz, *endo*-cyclopentyl), 0.17 (d, 3 H, J = 7 Hz, methyl); MS, m/e 262.1362 (calcd for $C_{19}H_{18}O$, m/e 262.1358).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.72; H, 6.74.

***exo*-3-Methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (15b).** To a −78 °C solution of 1.01 mmol of lithium diisopropyl amide[41] in 1.0 mL of dry ether was added dropwise a solution of 0.250 g (1.01 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one[3a] in 5.0 mL of dry ether. After the mixture was stirred for 20 min, 0.143 g (1.01 mmol) of iodomethane was added, and the mixture was stirred for 30 min at −78 °C. Neutral workup[41] with ether afforded 0.25 g of a yellow oil, which was chromatographed on a 1 × 30 cm silica gel column, eluted with 3% ether in hexane: fraction 1, 600 mL, nil; fraction 2, 100 mL, 80.0 mg (31%) of product alkylated bicycloketone as a clear oil; fraction 3, 200 mL, nil; fraction 4, 500 mL, 155.0 mg of unreacted starting ketone. The spectral data of the product *exo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were identical with the data from the minor product obtained via the photolysis of 4,4-diphenyl-6-methylcyclohex-2-enone.

Epimerization of *endo*-3-Methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (15a). A mixture of 50.0 mg (0.19 mmol) of *endo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 50.0 mg (0.47 mmol) of sodium carbonate in 10 mL of 1:1 dioxane–water was refluxed for 5 days. Neutral workup[41] with ether afforded 49 mg of a clear oil which was shown by ^{1}H NMR to be >95% of the *exo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

4,4-Diphenyl-6-propylcyclohex-2-enone (10).[42] To a refluxing solution of 12.3 mmol of isopropylmagnesium bromide[41] in 10.0 mL of THF was added dropwise a solution of 3.30 g (10.0 mmol) of 4,4-diphenylcyclohexenone cyclohexylimine[5a] in 7.0 mL of THF. The orange solution was refluxed for 1 h and cooled to room temperature before 3.00 g (25.0 mmol) of 1-bromopropane was added. The solution was stirred at room temperature for 1 h, slowly quenched with 20.0 mL of 10% hydrochloric acid, and stirred for 4 h. Neutral workup[41] with ether afforded 2.45 g of a yellow oil which was chromatographed on a 3 × 35 cm silica gel column: fraction 1, 2% ether in hexane, 750 mL, nil; fraction 2, 3% ether in hexane, 750 mL, nil; fraction 3, 4% ether in hexane, 750 mL, 0.54 g of product alkylated enone as a clear oil; fraction 4, 6% ether in hexane, 1000 mL, nil; fraction 5, 8% ether in hexane, 1000 mL, 0.45 g of starting enone. The product was recrystallized from ether in hexane to give 0.42 g (14%) of 4,4-diphenyl-6-propylcyclohex-2-enone, mp 145–146 °C.

The spectral data were the following: IR (neat) 3060, 3030, 2960, 2930, 2870, 1683 (C═O), 1600, 1495, 1450, 1385, 1235, 1190, 1060, 1035, 810, 755, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.1–7.4 (m, 11 H, arom and ═CH), 6.21 (d, 1 H, J = 10 Hz, ═CH), 2.74 (dd, 1 H, J = 12.5, 2.5 Hz, aliph), 2.41 (t, 1 H, J = 12.5 Hz, aliph), 2.25–2.4 (m, 1 H, aliph), 1.8–2.0 (m, 1 H, aliph), 1.2–1.5 (m, 3 H, aliph), 0.86 (t, 3 H, J = 7.5 Hz, methyl); MS, m/e 290.1679 (calcd for $C_{21}H_{22}O$, m/e 290.1671).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.43; H, 7.97.

Exploratory Direct Photolysis of 4,4-Diphenyl-6-propylhex-2-enone (10). A solution of 750 mg (2.58 mmol) of 4,4-diphenyl-6-propylcyclohex-2-enone in 250 mL of photograde benzene was irradiated under nitrogen[41,44] with a 450-W Hanovia medium-pressure mercury lamp through a sodium metavanadate filter solution[41] for 20 h. The photolysate was concentrated in vacuo to afford 750 mg of a light yellow oil which was shown by ^{1}H NMR to be free of starting enone. This photomixture was chromatographed on a 3 × 40 cm silica gel column: fraction 1, 2% ether in hexane, 1500 mL, nil; fraction 2, 4% ether in hexane, 400 mL, 319 mg (43%) of *exo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a clear oil; fraction 3, 4% ether in hexane, 200 mL, 420 mg (56%) of *endo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a clear oil.

The spectral data for *exo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (neat) 3065, 3035, 2965, 2940, 2878, 1725 (C═O), 1605, 1500, 1450, 1323, 1205, 1173, 1078, 1033, 770, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.2–7.4 (m, 10 H, arom), 3.12 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.70 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.60 (dd, 1 H, J = 13, 8 Hz, *exo*-cyclopentyl), 2.03 (dd, 1 H, J = 13, 9 Hz, *endo*-cyclopentyl), 1.5–1.65 (m, 1 H, α-ketocyclopentyl), 0.9–1.2 (m, 4 H, aliph), 0.71 (t, 3 H, J = 7 Hz, methyl); MS, m/e 290.1670 (calcd for $C_{21}H_{22}O$, m/e 290.1671).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.61; H, 7.80.

The spectral data for *endo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were the following: IR (neat) 3058, 3027, 2955, 2929, 2870, 1718 (C═O), 1603, 1495, 1447, 1320, 1213, 1188, 1154, 1076, 1029, 760, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.2–7.4 (m, 10 H, arom), 3.06 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 2.82 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 2.65 (t, 1 H, J = 13 Hz, *exo*-cyclopentyl), 2.3–2.5 (m, 1 H, α-ketocyclopentyl), 2.05 (dd, 1 H, J = 13, 5 Hz, *endo*-cyclopentyl), 0.9–1.1 (m, 4 H, aliph), 0.61 (t, 3 H, J = 7 Hz, methyl); MS, m/e 290.1670 (calcd for $C_{21}H_{22}O$, m/e 290.1671).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.59; H, 7.70.

***exo*-3-Propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (16b).**[42] To a refluxing solution of 2.92 mmol of isopropylmagnesium bromide[41] in 5.0 mL of THF was added dropwise a solution of 0.80 g (2.43 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one cyclohexylimine[5] in 5.0 mL of THF. The solution was refluxed for 1 h and cooled to room temperature before 1.20 g (9.7 mmol) of 1-bromopropane was added. The solution was stirred at room temperature for 2 h, quenched with 20 mL of 5% hydrochloric acid, and stirred for 1 h. Neutral workup[41] with methylene chloride afforded 460 mg of an orange oil which was chromatographed on a 2 × 30 cm silica gel column eluted with 2% ether in hexane: fraction 1, 1000 mL, nil; fraction 2, 400 mL, 140 mg of alkylated bicycloketone as a clear oil. The spectral data were identical with the data from the minor product obtained via photolysis of 4,4-diphenyl-6-propylcyclohex-2-enone.

Epimerization of *endo*-3-Propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (16a). A mixture of 25.0 mg (0.09 mmol) of *endo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 25.0 mg (0.24 mmol) of sodium carbonate in 18.0 mL of 5:1 THF–water was refluxed for 48 h. Neutral workup[41] with ether afforded 25 mg of a clear oil which was shown by ^{1}H NMR to be >90% of the *exo*-3-propyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Summary of Quantum Yield Results for C-6 Substituted 4,4-Diphenylcyclohex-2-enones 6–10. All direct, sensitized, and quenched quantum yield determinations were performed using the microoptical bench[8] employing an Osram HBO 200-W high-pressure mercury lamp and a Bausch and Laumb Model 33-86-79 monochromator with a 5.4 mm entrance slit and a 3.0 mm exit slit. Light output was measured with digital electronic actinometry,[9] and all runs were calibrated with ferrioxalate actinometry.[10] The direct and sensitized runs were purged with purified nitrogen[41,44] for 1 h prior to and during photolysis; however, due to the volatility of 1,3-cyclohexadiene, the quenched runs were only purged 1 h prior to the addition of quencher and subsequent photolysis. Analysis was done by HPLC eluting with 2 to 4% ethyl acetate in hexane with recrystallized 4-methoxybenzophenone or 4,4′-dimethoxybenzo-

Table VII. Summary of Viscosity-Dependent Quenching Runs

run no.	solvent	viscosity[a]	solvent molarity[b]	[Q][c]	light[d] abs. (mE)	conv (%)	ϕ[e]	$1/k_q\tau$[e]
1	hexane	0.313	7.66	0.00	0.640	3.7	0.0324	
2	hexane	0.313	7.66	0.10	0.455	0.7	0.0090	0.0348[f]
3	hexane	0.313	7.66	0.20	0.629	0.5	0.0047	
4	methylcyclohexane	0.734	7.84	0.15	0.626	0.9	0.0078	0.0476[g]
5	cyclohexane	0.980	9.25	0.25	0.629	0.6	0.0055	0.0511[g]
6	*n*-dodecane	1.508	4.40	0.15	0.428	0.7	0.0090	0.0577[g]

[a] Viscosities at 20 °C taken from ref 17c. [b] Calculated from solvent densities at 20 °C taken from ref 17c. [c] Concentration of 1,3-cyclohexadiene, M. [d] Irradiation at 366 nm. [e] Error = ±10%. [f] Value taken from slope of the Stern–Volmer plot. [g] Value obtained from a single point.

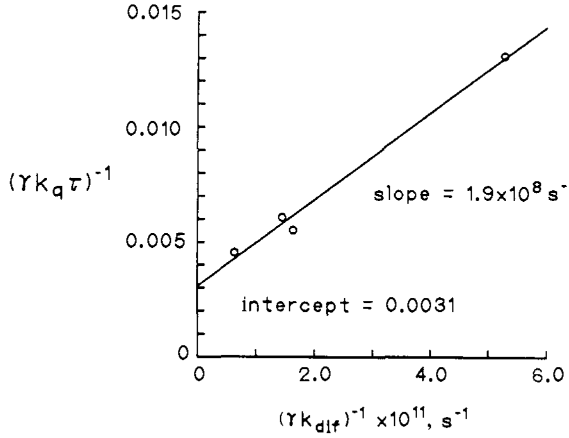

Figure 6. Viscosity data plotted according to Saltiel's method.

phenone as a standard. The runs are summarized in Tables X–XIII of the Supplementary Material.

Viscosity-Dependent Quenching of 4,4-Diphenylcyclohexenone. Quantum yields for the quenching of the photoreaction of 4,4-diphenylcyclohexenone to *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one by 1,3-cyclohexadiene were determined in photograde solvents:[41] *n*-hexane, methylcyclohexane, cyclohexane, and *n*-dodecane. The microoptical bench apparatus[8] was used as described above. Each run was done at 20 °C in a 42-mL solution which was purged for 1 h prior to addition of quencher and subsequent photolysis at 366 nm. Analysis was done with HPLC eluting with 5% ethyl acetate in hexane with 4,4′-dimethoxybenzophenone as a standard.

The unquenched quantum yield, ϕ_0, in *n*-hexane was determined to be 0.032, which was within experimental error of that observed from previous work.[3e] Quenched quantum yields, ϕ, at quencher concentrations of 0.10 and 0.20 M were also determined in *n*-hexane and the data resulted in a linear Stern–Volmer plot ($\phi_0/\phi = 1 + k_q\tau[\mathrm{Q}]$). Previous work[3e] revealed that ϕ_0 was the same in *n*-hexane and *n*-dodecane and ϕ_0 was taken equal to 0.032 for the other cycloalkane solvents. Four points were obtained in dodecane from our previous study[3e] and two-point plots were used in methylcyclohexane and cyclohexane. The inverse values of these $k_q\tau$ values were used to construct the plot in Figure 3 of the Results Section. The runs are summarized in Table VII.

Alternative Treatment of Viscosity-Dependent Quenching Data. As described in the Results Section, the viscosity-dependent quenching data from above were utilized to determine the triplet lifetime and the bimolecular rate constant for energy transfer. The method used was similar to that previously applied to the triplet quenching of valerophenone by Wagner and Kochevar.[18a] The treatment requires two assumptions involving the solvent independence for (1) the triplet lifetime and (2) γ, the ratio of $k_{-\mathrm{dif}}/k_{\mathrm{dif}}$. Although assumption 1 appears reasonable, Saltiel[18b,c] has questioned assumption 2.

Instead, Saltiel has proposed that γ is entirely determined by the cratic entropy[46] for formation of the donor–acceptor encounter pair, i.e. γ equals the solvent molarity. Hence, a plot of $(\gamma k_q\tau)^{-1}$ vs $(\gamma k_{\mathrm{did}})^{-1}$ should be linear with a slope equal to $1/\tau$ and an intercept equal to $1/(\tau k_{\mathrm{ET}})$ (see eq 6a in the Results Section). For each solvent k_{dif} is calculated from the Debye equation.[17] The plot of $(\gamma k_q\tau)^{-1}$ vs $(\gamma k_{\mathrm{dif}})^{-1}$ for the data from Table VII is presented in Figure 6. From the slope, the lifetime is calculated to be 5.3 ns, which can be used with the intercept to obtain k_{ET} equal to 6×10^{10} s^{-1}. The lifetime is shorter than that derived above (8.3 ns), and thus k_{ET} is found to be greater than the 1.6×10^{10} value obtained previously.

The value for k_{ET} along with the solvent molarity and viscosity can be used to calculate values for k_q in each solvent (see eq 6a in the Results Section). These values have been included in Table III above. The values for k_q in aliphatic solvents from this method are somewhat greater than those afforded from the previous method. However, each treatment results in nearly the same rate constant for quenching in benzene, ca. 3×10^9 M$^{-1}\cdot$s^{-1}.

Table VIII. CI State Energies for Diphenyl Enone Rearrangement

reaction coordinate[a]		state energies (heat of formation), kcal/mol	
type	angle	singlet, S_0	triplet, T_1
A	105	48.6641	115.3125
A	100	48.4531	115.5547
A	95	49.7578	117.8203
A	90	52.5625	113.8672
A	85	56.9922	121.1875
A	80	62.5000	122.7031
A	75	69.6016	118.4063
A	70	78.0547	113.1953
A	65	86.8906	106.0938
A	60	95.0078	100.8750
A	55	99.8750	99.8750
A	50	89.8516	82.5391
A	45	73.3828	69.0469
A	40	63.0234	60.2656
A	35	58.4766	55.9453
A	30	59.8215	57.0156
A	25	67.0469	63.6875
B	110	72.3516	66.8594
B	100	64.4141	66.0938
B	90	61.5469	73.9922
B	80	59.5625	94.0469
B	70	39.1406	101.5859
B	60	30.2188	99.7422

[a] Angle in degrees; A = C-3-C-4-C-7, B = C-2-C-3-C-4.

UV Absorption and Fluorescence Emission Measurements. The ultraviolet absorption spectra for both the naphthylbutyl and naphthylmethyl enones, **6** and **7**, were essentially the same as that of an equimolar mixture of 4,4-diphenylcyclohexenone and 2-methylnaphthalene, i.e., a summation of the absorption spectra of the separate enone and naphthyl chromophores. For each case: UV (0.001 M in benzene) $\lambda_{\max}$ 309 nm (ϵ 630), 315 nm (ϵ 400), 322 (ϵ 600); UV (1.2×10^{-4} M in absolute ethanol) $\lambda_{\max}$ 268 nm (ϵ 5670).

Fluorescence measurements were made on an Aminco-Kiers spectrophosphorimeter equipped with a Hanovia 901C-1 150-W xenon arc lamp, modified with internal baffles to eliminate scatter, and interfaced to a PDP 11/55 microcomputer. The fluorescence spectra were obtained from absolute ethanol solutions at 295 K. The concentrations (ca. 10^{-4} M) were adjusted to give an optical density in the range of 0.5–0.8. The excitation wavelength used in all cases was 270 nm. Fluorescence was observed from reference solutions of 2-methylnaphthalene and an equimolar mixture of 4,4-diphenylcyclohexenone and 2-methylnaphthalene. In contrast, solutions of the same concentration of either the naphthylmethyl enone or the naphthylbutyl enone gave no fluorescence (less than 1000 times weaker than that observed from the reference solutions).

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with the MMP2[23] program. Where torsional or bending constants were not available, constants approximating them were employed. For the species in which a phenyl group is half-migrated, the spiro system was treated as a cyclopropane ring and the odd-electron centers (i.e. the para carbon in the migrating phenyl group and the carbon-2 of the enone system) were treated as sp^2 carbons.

Quantum Mechanics Calculations. Quantum mechanics calculations were performed with the "MOPAC" program package[39a] utilizing the MNDO approximation.[39b]

The hypersurface for the rearrangement of 4,4-diphenylcyclohexenone to *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was obtained by first varying the C-3-C-4-C-7 angle (ϕ_A) in 10° increments from 105° in the starting enone structure (Figure 7a) to 25° in the 1,3-diradical (Figure

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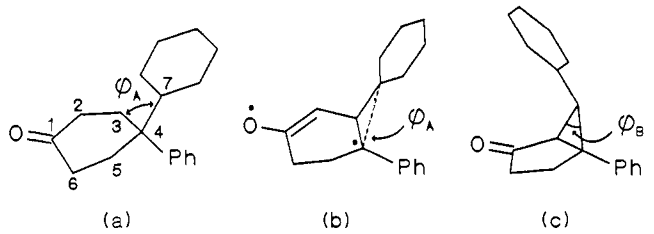

Figure 7. Reaction coordinate definitions for the diphenyl enone system: (a) starting enone; (b) intermediate 1,3-diradical; (c) bicyclic photoproduct.

Table IX. CI State Energies of Twisted Cyclohexenone

	state energies (heat of formation), kcal/mol		
dihedral angle[a]	singlet, S_0	triplet, (π–π^*)	triplet, (n–π^*)
0	-42.6055	3.5293	27.9023
30	-38.3438	-0.5605	34.7012
60	-23.8184	-1.4160	46.1230
90	7.6035	9.8496	65.9316
120	62.6563	48.7656	106.5957

[a] C-1–C-2–C-3–C-4 angle in degrees.

7b). The reaction surface was completed by starting with the optimized product structure (Figure 7c) and then opening the C-2–C-3–C-4 angle (ϕ_B) in 10° increments from 60° to 110°. In order to minimize computation time, the geometries were obtained via ground state optimization using the reaction coordinates mentioned above. The bond lengths, angles, and dihedral angles within the nonmigrating phenyl were fixed to values found in benzene, although the ipso carbon–C-4 bond was optimized and this phenyl ring was allowed to rotate. Single SCF calculations including four-electron configuration interaction were performed on each of these optimized structures to first obtain the energy of the ground state, S_0, and then that of the lowest triplet state, T_1. By inspection of the triplet SCF molecular orbitals and their configuration interaction mixing, this triplet state was found to be an n–π^* state. The state energies are summarized in Table VIII.

In addition, the effect of α–β double bond twisting of the unsubstituted cyclohex-2-enone was also investigated. The C-1–C-2–C-3–C-4 dihedral angle (cyclohexenone numbering) was varied while fully optimizing for both the ground state and lowest triplet state geometries. The state energies for the ground state, S_0, and two lowest triplet states were obtained from these geometries with a six-electron configuration interaction calculation. These are listed in Table IX. Unlike the diphenyl enone case above, the lowest triplet was found to be a π–π^* state. These results are similar to those obtained in a previous calculation.[47]

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Registry No. 4, 4528-64-7; **5**, 118017-43-9; **6**, 118017-44-0; **7**, 118017-45-1; **8**, 118017-46-2; **9**, 42420-87-1; **10**, 42420-91-7; **12a**, 118017-47-3; **12b**, 118100-96-2; **13a**, 118017-48-4; **13b**, 118100-97-3; **14a**, 118017-49-5; **14b**, 118100-98-4; **15a**, 118017-50-8; **15b**, 118100-99-5; **16a**, 118017-51-9; **16b**, 118101-00-1; *endo*-**19** (R = Me), 118070-28-3; *exo*′-**19** (R = Me), 118070-27-2; *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one cyclohexylimine, 118017-42-8; 4-(2-naphthyl)-1-bromobutane, 2657-45-6; 2-(bromomethyl)naphthalene, 939-26-4; *trans*-2,6-diphenylbicyclo[3.1.0]hexan-2-one, 21414-81-3; 4-(chloromethyl)biphenyl, 1667-11-4; 4-(bromomethyl)biphenyl, 2567-29-5; 1-bromopropane, 106-94-5; cyclohexadiene, 29797-09-9.

Supplementary Material Available: Kinetic analysis of bichromophoric naphthylalkyl enones and tables of quantum yield data for **6**, **7**, **8**, and **10** and positional parameters, interatomic distances, bond angles, and anisotropic and isotropic temperature factors for **14b** (10 pages). Ordering information is given on any current masthead page.

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(47) Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5160-5167.

An Assortment of Highly Unusual Rearrangements in the Photochemistry of Vinylcyclopropanes. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: The singlet and triplet photochemistry of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane was investigated. In the (diphenylvinyl)cyclopropane case, direct irradiation led via the singlet excited state to three isomers along with Griffin fragmentation products. Interestingly, the three isomers arose from fission to afford the less stable of two alternative allylic diradicals. Two of the isomers arose from unique rearrangements of the allylic diradical wherein the allylic moiety closes 1,3 and C-2 of this group either bonds to a second odd-electron center or abstracts a hydrogen. The third isomer resulted from ring opening and hydrogen transfer. In the case of the (dicyanovinyl)cyclopropane direct irradiation gave rise to a reverse di-π-methane rearrangement involving bicycling of a divalent carbon species along a π-system. Additionally, the hydrogen transfer process observed for the (diphenylvinyl)cyclopropane was again encountered. As in the case of the (diphenylvinyl)cyclopropane, there was a preference for products derived from the less stable of two alternative diradicals. The partition between the reverse di-π-methane rearrangement and the hydrogen transfer process proved solvent dependent with the latter being favored in polar solvents. The triplet of the (dicyanovinyl)cyclopropane again opened to the less stable of two diradicals and this underwent an unprecedented regioselective phenyl migration. Quantum yields were obtained for the reactions of interest.

In the mid-1960's we described several examples[3] of the di-π-methane rearrangement.[4,5] In one of these early studies[3c] secondary photochemistry of the vinylcyclopropane product was encountered. In more recent studies of vinylcyclopropanes having

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(1) This is Paper 155 of our photochemical series and Paper 215 of the general series.

(2) For Paper 154 see Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.*, preceding paper in this issue.