Photochemistry of a Biphenylyl-Substituted Cyclohexenone—Mechanistic and Exploratory Organic Photochemistry[1,2]

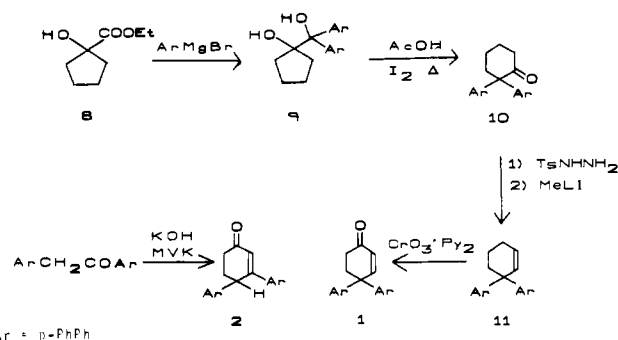Howard E. Zimmerman,* Xu Jian-hua, Russell K. King, and Craig E. Caufield

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Abstract: The photochemistry of 4,4-dibiphenylylcyclohexenone was investigated in order to ascertain the effect of having the chromophore at carbon-4 equal in T_1 energy to the enone moiety. Direct irradiation led to the cis and trans isomers of 5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one and also 3,4-dibiphenylylcyclohex-2-en-1-one. The quantum yields in *tert*-butyl alcohol were 0.26 for trans product, 0.024 for cis product, and 0.020 for 3,4-enone. In benzene the quantum yields were 0.33, 0.019, and 0.013, respectively. Exothermic sensitization with xanthone ($E_T = 74$ kcal/mol) and isoenergetic sensitization with benzophenone ($E_T = 69$ kcal/mol) led to the same products and with the same quantum yields as in the direct photolyses. In contrast, endothermic sensitization with thioxanthone ($E_T = 65$ kcal/mol) afforded the same product distribution but with diminished quantum efficiency. The direct quantum yields were independent of wavelength. It was concluded that equilibrating triplet excited states are responsible for the photochemistry encountered which thus qualitatively parallels the photochemistry of 4,4-diphenylcyclohexenone. The rates of triplet rearrangement and of triplet decay were determined by quenching studies. It was ascertained that the rate of rearrangement was 1.3×10^8 s^{-1} (benzene) while the total triplet decay was 3.4×10^8 s^{-1}. Accordingly, the triplet rearrangement rate was nearly sixfold more rapid than in the phenyl series, while triplet decay was somewhat less than twofold slower. The net result was an enhanced quantum efficiency of the reaction corresponding to a factor of 8 (benzene). The mechanisms and electronic effects are discussed.

One of our continuing research interests has been the photochemistry of cyclohexenones. It appeared of considerable interest to investigate the behavior of 4,4-diarylcyclohexenones having aryl groups of varying triplet energies relative to that of the 69 kcal/mol[3] enone moiety. In the present study, biphenylyl was selected, since this group has a triplet energy of ca. 69 kcal/mol,[4–7] approximately equal to that of the enone chromophore.

Further, the behavior of bichromophoric excited states has been of increasingly general interest,[8,9] and the present studies had additional interest in the expectation that reaction resulting from excitation of the C-4 aryl group would be more akin to a di-π-methane rearrangement while reaction originating from excitation

(1) This is paper 144 of our Mechanistic and Exploratory Organic Photochemical Series and 202 of our general papers.

(2) For paper 143 note: Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539.

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

(4) (a) In our earlier efforts on cyclohexenone photochemistry we noted that T_1 of biphenyl was possibly higher than the then accepted 65 kcal value and that biphenyl is a nonvertical energy acceptor.[4b] (b) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965–1973.

(5) (a) An earlier estimate had been made as 65 kcal/mol[5b–d]; (b) Clar, I. E. *Chem. Ber.* **1956**, *89*, 749–762. (c) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *53*, 1042–1052. (d) Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100–2116.

(6) (a) Subsequently, Wagner[6b] has concluded that the 0–0 energy for biphenyl triplet is 69 kcal/mol. (b) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820–2825.

(7) (a) This corresponds to the 0–0 energy. S_0 is nonplanar while due to the larger π-bond order between phenyl groups T_1 is planarized. (b) One may well expect lower than diffusion controlled energy transfer in the biphenyl case.[7c] (c) Wagner, P. J., private communication.

(8) (a) Note ref 8b and 8c for reviews. (b) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383–389. (c) DeSchryver, F. C.; Boens, N. *Adv. Photochem. 10*, 359–465. (d) For examples of recent reports of photochemistry of bichromophoric systems note ref 8c and e. (e) Morrison, H.; Miller, J. *Am. Chem. Soc.* **1983**, *105*, 2398–2408.

(9) (a) One of the simplest and oldest examples of a reaction of a bichromophoric system is the di-π-methane rearrangement. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (c) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727. (d) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

Scheme I. Synthesis of Photoreactant and a Photoproduct

of the enone moiety would be similar to the 4,4-diphenylcyclohexenone example[3] we studied previously.

Results

Syntheses of the Photochemical Reactant and Potential Photoproducts. Scheme I outlines the synthesis of the required 4,4-dibiphenylylcyclohex-2-en-1-one (1); details are given in the Experimental Section. Also, it seemed worthwhile to prepare 3,4-dibiphenylylcyclohex-2-en-1-one (2), since its counterpart had been encountered in our earlier study.[3] This is included in Scheme I.

Exploratory Photochemistry of the Dibiphenylylcyclohexenone and Photoproduct Structure Elucidation. In exploratory photolyses of the dibiphenylylcyclohexenone 1 three photoproducts, A, B, and C, were observed. Since in our earlier studies[3] on the photochemistry of 4,4-diphenylcyclohexenone (3) the products were

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

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

(12) (a) A number of investigators[3,10,11,12b–e] have observed three-ring opening of cyclopropyl ketones in alkali metal–liquid ammonia. (b) Norin, T. *Acta Chim. Scand.* **1965**, *19*, 1289–1292. (c) Nickon, A.; Kwasnik, H.; Swartz, T.; Williams, R. O.; Digorgio, J. B. *J. Am. Chem. Soc.* **1965**, *87*, 1615–1617. (d) Volkenburgh, R.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1949**, *71*, 3595–3601. (e) Dauben, W. G.; Deviny, E. J. *J. Org. Chem.* **1966**, *31*, 3794–3798.

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Table I.[a] Comparison of Selected Portions of the NMR Spectra (δ) of the Diphenyl and the Dibiphenylyl 5,6-Substituted Bicyclo[3.1.0]hexanones

peak	cis-dibiphenylyl	cis-diphenyl		trans-dibiphenylyl	trans-diphenyl	
1	2.30	2.30		1.08	0.96	
2	2.38	2.39	A_2B_2	1.16	1.07	part of
3	2.48	2.48	multiplet	1.25	1.16	A_2B_2
4	2.52	2.52		1.36	1.24	sextet
5	2.62	2.62		1.40	1.32	
6				1.46	1.38	
7				1.72	1.78	A_2B_2
8				1.96	1.96	triplet
9				2.04	2.03	A_2B_2
10				2.08	2.08	
11-17				septet	septet	
18	2.66	2.66		2.64	2.66	
19	2.69	2.69	AB	2.73	2.76	AB
20	2.84	2.84	quartet	3.07	3.10	quartet
21	2.88	2.88		3.16	3.20	

[a] Only aliphatic absorptions are included.

the stereoisomeric 5,6-diphenylbicyclo[3.1.0]hexanones (**4a,b**) and also the 3,4-diphenylcyclohex-2-en-1-one (**5**), analogous products seemed probable in the present study. Indeed, the NMR spectra of two of the photoproducts, A and B, were quite similar to the spectra of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexanones (**4a,b**). This is clear from inspection of Table I.

One attractive approach towards determination of structure utilized the lithium–liquid ammonia reduction of bicyclo-[3.1.0]hexanones[10-12] in which the three-membered ring was observed to be opened. Lithium–liquid ammonia reduction of photoproduct A, thought from NMR to be *trans*-5,6-dibi-phenylylbicyclo[3.1.0]hexan-2-one (**6a**), led to a dihydro product **7**, mp 155–156 °C, which exhibited a carbonyl stretching frequency in the infrared at 1705 cm⁻¹ suggestive of a cyclohexanone.

Confirmation was obtained with an independent synthesis of *cis*-3,4-dibiphenylylcyclohexanone (**7**), which proved identical with the lithium–liquid ammonia degradation product as outlined in Scheme II.

Hence, photoproduct A can, indeed, be assigned the structure of *trans*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one (**6a**).

Beyond proving the structure of photoproduct A, these efforts established the structure of photoproduct C, since the synthetic 3,4-dibiphenylylcyclohex-2-en-1-one (**2**) was identical with this photoproduct.

Photoproduct B had an NMR spectrum which was nearly identical with that of the known *cis*-5,6-diphenylbicyclo[3.1.0]-hexanone (**4a**) (note Table I), hence suggesting that this photoproduct was the *cis*-5,6-dibiphenylyl bicyclic ketone **6b**. This conclusion was supported by the photochemical cis–trans interconversion described below. Finally, definitive evidence was obtained from the lithium–liquid ammonia reduction of photoproduct B which led to 2-(biphenylylmethyl)-3-biphenylylcyclopentanone **12**. The latter, **12**, was independently synthesized as depicted in Scheme II.

With the structure of the photoproducts established, the irradiation of 4,4-dibiphenylylcyclohexenone **1** can be depicted as in eq 1.


Ar = p-PhPh
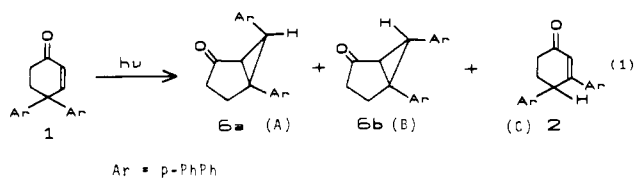
Photoproduct Isomerization. In our studies[3,10] of the phenyl analogues of the present photochemistry it was observed that the stereoisomeric bicyclo[3.1.0]hexanones **4a,b** interconverted photochemically. Hence it was important to ascertain if the same behavior resulted in the biphenylyl system. Furthermore, the isomerization promised to add weight to the structural assignment made for photoproduct B.

Scheme II. Photoproduct Degradation and Related Syntheses

Ar = p-PhPh
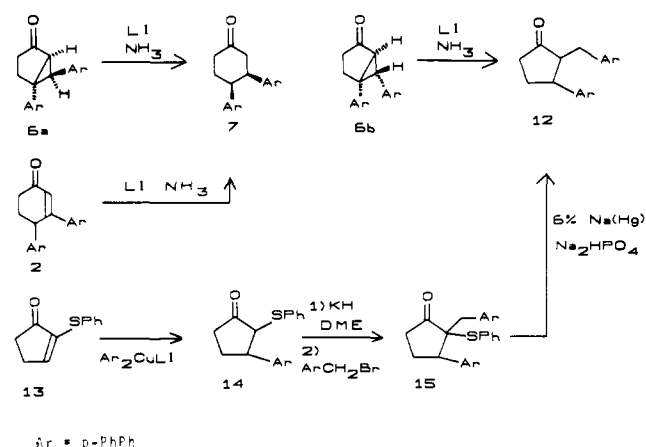
Indeed, it was observed that the *cis*- and *trans*-5,6-dibi-phenylylbicyclic ketones, **6b** and **6a**, were interconverted. The cis–trans interconversion is depicted in eq 2.

Ar = p-PhPh
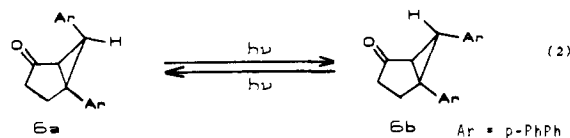
This equilibration of the bicyclic stereoisomers, however, did not give an erroneous kinetic ratio of **6a** to **6b** or inaccurate quantum yields in the enone photolysis, since the primary photochemistry was extrapolated to 0% conversion (vide infra).

Enone Reaction Multiplicity, Quantum Yield, and Rate Studies. Our next effort dealt with the matter of quantum yields and reaction multiplicity. Direct, sensitized, and quenched quantum yields were run to varying extents of conversion ranging from 8.2% to 1.6%. Note the Experimental Section for details. The efficiencies were found to be a weak function of the extent of conversion. Table II summarizes the values extrapolated to zero conversion. A further point of interest was the observation that the efficiencies of formation of the bicyclic products were independent of which wavelength, 280 or 325 nm, was employed, although in the former case essentially all of the light is captured by the biphenylyl group while in the latter virtually all is absorbed by the enone moiety.

It is seen that as the sensitizer energies were increased the quantum yields in the sensitized runs approached the 0.26 value of the direct irradiation (entry 1 of Table II). With the T_1 energies of the biphenylyl[6] and the enone[3a] moieties both being 69 kcal/mol, it is not surprising that the lower energy sensitizer thioxanthone (E_T = 66 kcal/mol[13]) transfers triplet excitation inefficiently. That this diminished efficiency is not due to the thioxanthone lifetime being too short compared with the rate of diffusion derives from two sources. First, the 77-μs lifetime reported[13] for thioxanthone together with the 0.005 M enone concentration affords a prediction of a pseudo-unimolecular collision rate of circa 3×10^7 s⁻¹ compared with the 1.3×10^4 s⁻¹ decay rate. Secondly, at similar acceptor concentrations, unit efficiencies have been observed for enones and dienones having naphthyl rather than biphenylyl groups.[14] Despite the inefficient energy transfer, this low-energy sensitizer (i.e., thioxanthone) does give the same product distribution, within experimental error, as the higher-energy sensitizers.

Having used sensitization studies independently to generate and determine the behavior of the triplet 4,4-dibiphenylyl enone **1**, we proceeded to investigate the nature of the rearranging species in the direct irradiations. This was done with quenching studies to determine whether or not there was a quenchable triplet, and

(13) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777.

(14) (a) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732–7744. (b) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.

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Table II. Quantum Yield Summaries[a]

		quantum yield		
type of run	sensitization energy	trans bicyclic	cis bicyclic	3,4-enone
direct[b,e]	d	0.26	0.024	(0.020)
direct[b,f]	d	0.20	0.015	0.023
direct[c,e]	d	0.33	0.019	0.013
xanthone sensitizer[b]	74 kcal	0.26	0.021	0.021
benzophenone sensitizer[b]	69 kcal	0.24	0.023	0.020
thioxanthone sensitizer[b]	66 kcal	0.061	0.005	0.005

[a] Zero-time, extrapolated values. [b] Run in *tert*-butyl alcohol. [c] Run in benzene. [d] Not applicable. [e] 325 NMR irradiation. [f] 280-nm irradiation.

also to provide the rates of triplet rearrangement and decay.

Since the triplet energies of the two chromophores in dibiphenylyl enone **1** are 69 kcal/mol, cyclohexadiene with a 53 kcal/mol triplet energy[15] was expected to quench the enone triplets with a diffusion-controlled rate.[3a]

It was found that the dibiphenylyl enone rearrangement was, indeed, quenched with cyclohexadiene, thus demonstrating the presence of a reacting triplet. A Stern–Volmer plot of ϕ_0/ϕ vs. quencher concentration is given in Figure 1. As usual, the slope gives us operational values (vide infra) of $k_q/k_{d(tot)}$ as well as the lifetime (i.e., $\tau = 1/k_{d(tot)}$) (also note below). Also, k_r can be obtained from solution of $\phi = k_r/k_{d(tot)}$. Here k_r is an operational rate constant giving the overall rate of triplet utilization multiplied by the probability of triplet reaction; this point also is discussed further below. The values obtained are summarized in Table III.

Interpretative Discussion

Reaction Multiplicity and Efficiency. The first point we note is the strikingly high efficiency of the direct and sensitized rearrangements of the dibiphenylyl enone **1** compared with the photochemistry of 4,4-diphenylcyclohexenone (**3**). The quantum efficiencies are 0.30 (*t*-BuOH) and 0.36 (benzene) which is ca. four times the 0.078 efficiency[3a] observed for the diphenyl analogue **3** in *tert*-butyl alcohol and ca. eight times the 0.043 value in benzene.

The second point of interest deals with the reaction multiplicity. We note that the same quantum efficiencies are obtained on direct irradiation as with xanthone (E_T = 74 kcal/mol) or benzophenone (E_T = 68.5 kcal/mol) sensitization; note Table II. The identity of direct and sensitized efficiencies holds for all of the photoproducts.

This recalls the "fingerprint method of identification"[3a,11,17] which we put forth over a decade ago. It was suggested that when two reactions afford the same distribution of products, this provides a "fingerprint" comparison which allows one to conclude that there is a species common to both reactions. If one of the reactions has an identified species, such as a triplet generated in the present sensitized photolyses, then the second reaction—here the direct irradiation—can be assumed to proceed via the same intermediate.

Beyond this, obtaining the same quantum yields in the direct and the sensitized runs indicates that the intersystem crossing efficiency in the direct irradiations must be unity.

The lower quantum yields obtained with thioxanthone (E_T = 66 kcal/mol) are most reasonably attributed to the somewhat endothermic energy transfer required. In an early example,[3a] it was observed that the efficiency of enone triplet quenching was a function of (inter alia) the exothermicity of energy transfer from enone triplet to quencher. An energy requirement was encountered larger than the 3-kcal/mol value originally postulated by Porter
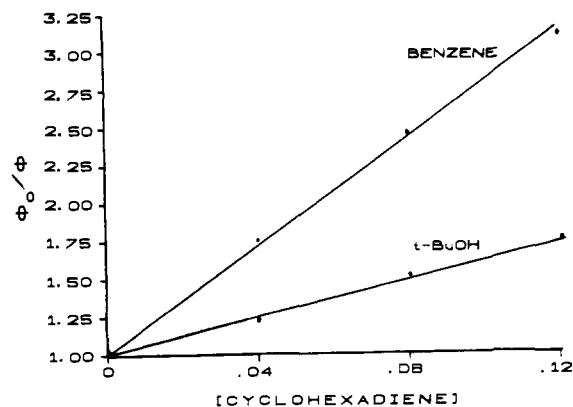

Figure 1. Quenching of the dibiphenylyl enone rearrangement.

Table III. Summary of 4,4-Dibiphenylyl Enone Rate Constants[a]

solvent	τ, ns	$k_{d(tot)}$, s^{-1}	k_r, s^{-1}
t-BuOH	3.08	3.3×10^8	1.1×10^8
benzene	2.90	3.4×10^8	1.3×10^8

[a] These assume rates of diffusion and quenching in *t*-BuOH and benzene respectively of 2.9×10^9 and 6.0×10^9 s^{-1}.[16]

and Wilkinson[18,19] for diffusion-controlled quenching.

Equation 3[20] gives the sensitized efficiency as a function of the various rate constants in reversible energy transfer, reaction, and decay. Here k_{ET} is the rate of energy transfer from sensitizer,

$$\phi_{sens} = \phi_r \left[\frac{1 + k_{ET}R\tau_s}{1 + k_{ET}R\tau_s + k_{-ET}S\tau_r} \right] \quad (3)$$

of concentration S, to reactant, of concentration R. k_{-ET} is the rate of back transfer, and the τ's are the triplet lifetimes. It is seen that efficient transfer will occur when $k_{ET}R\tau_s$ is large and $k_{-ET}S\tau_r$ is small. The former results when the forward rate of energy transfer is large compared with the rate of sensitizer decay. The latter results when the back energy transfer is slow compared with the total rate of decay of reactant triplet.

Significance of the Measured Efficiencies, Lifetimes, and Rates. In our previous studies of 4,4-diphenylcyclohexenone, the enone moiety selectively absorbed the incident light, was converted by intersystem crossing to triplet multiplicity, and then induced migration of a phenyl group. Not only the singlet but also the triplet excitation energy of the enone chromophore is much lower than that of the phenyl groups, and electronic excitation is anticipated to be concentrated in the enone moiety.

More generally, as in the present study, more than one chromophore may possibly be excited. On the basis of extinction coefficients the expectation is that in the 280-nm runs the biphenylyl group in enone **1** captures essentially all of the incident light. At wavelengths above 300 nm the enone moiety absorbs progressively more heavily. In the 325-nm runs essentially all of the light is absorbed by the enone chromophore. Nevertheless, the enone moiety should be of lower singlet energy (ca. 76 kcal/mol[21a]) compared with an isolated biphenyl moiety (99 kcal/mol[21b]). Thus the observed wavelength independence is not unexpected, since any singlet excitation initially in the biphenyl moiety would most likely rapidly be transferred to the enone chromophore. That such energy transfer is rapid has precedent in our study[22] of singlet transfer in rod-like molecules from

(15) Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4781–4782.

(16) (a) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238. (b) Wagner, P. J.; Spoerke, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4437–4440. (c) Scaiano et al. (Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539–1542) have reported a value of 6.0×10^9 L M^{-1} s^{-1} for the quenching of *p*-methoxyacetophone by oxygen in benzene and similar values for analogous quenching of various ketones by dienes in this solvent.

(17) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966.

(18) Porter, G.; Wilkinson, F. *Proc. R. Soc. London* **1944**, *66*, 2100–2109.

(19) Wilkinson, F. *J. Phys. Chem.* **1962**, *66*, 2569–2574.

(20) Wagner, P. J. In "Creation and Detection of the Excited State"; Lamola, A. A., Ed.; Dekker, Inc.: New York, 1971; pp 173–212.

(21) (a) Torri, J.; Azzaro, M. *Tetrahedron Lett.* **1973**, *3251*–3253. (b Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1965.

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

naphthyl to acetyl or benzoyl groups ca. 7 Å distant; these rates were above 10^9 s^{-1}. Further, very facile intersystem crossing at the enone end of the molecule should follow as a consequence of spin–orbit coupling at the carbonyl group. Hence at time zero for generation of the triplet from direct irradiation, excitation seems most likely to be localized in the enone end of the molecule. This has parallel in other studies.[14b]

Several points require comment. One is the assignment of 69 kcal/mol to the enone triplet involved in the rearrangement. Recently, evidence in the form of a laser-detected transient has been presented[23,24] for the presence of a 61–63 kcal/mol cyclohexenone triplet. A twisted enone structure has been suggested for this species. However, Schuster, Bonneau, and Joussot-Dubien[23a] as well as Pienta[24] have reported that this triplet is not quenched by cyclohexadiene and is most likely not responsible for the type A cyclohexenone rearrangements.[25] In parallel, it seems not to be the same triplet configuration as that responsible for the presently studied enone rearrangements where an aryl group migrates, since these are quenched by cyclohexadiene. Related to this first point is the choice of the rate of quenching of the excited moieties. Since the laser-detected transient does not correspond to the one quenched by cyclohexadiene and leading to reaction, the rate of the reactive cyclohexenone triplet moiety quenching in the presently studied molecule must be more rapid than the slow quenching rate of the twisted triplet. Ketone quenching by cyclohexadiene in benzene is taken as 6×10^9 s^{-1} on the basis of rates of quenching by dienes in a variety of literature studies.[16] Hence, until and unless further evidence indicates that a longer-lived and more slowly quenched twisted triplet is reacting rather than the untwisted n–π* triplet, it seems wise to assume diffusion control in quenching.

A related observation is the inefficient energy transfer from thioxanthone (66 kcal/mol) to biphenylyl enone **1**. This contrasts with very efficient transfer to comparable naphthyl enones and dienones we have studied. If a 61–63 kcal/mol enone triplet, capable of reaction, were available, one might anticipate similar efficient sensitization except possibly for inhibition by the nonvertical nature of the energy transfer to a twisted enone triplet.

We now need to consider whether certain observations are helpful in determining the nature of the reaction. These observations are (i) lack of wavelength dependence on direct irradiation, (ii) the independence of efficiency on direct vs. sensitized irradiation, (iii) the constancy of product ratio despite varying sensitizer energy, and (iv) the linearity of the quenching curves. We also need to consider the significance of the efficiencies, rates, and lifetimes obtained.

In the general case, the kinetics are as shown in Scheme III. Here E is the molecule with a triplet excited enone moiety and X is the molecule with a triplet excited aryl group.

For simplicity we define the following quantities.

$$K_e = k_{re} + k_{de} \tag{4a}$$

$$K_x = k_{rx} + k_{dx} \tag{4b}$$

$$L_x = I_x/I \text{ and } L_e = I_e/I, \text{ while } L_e + L_x = 1 \tag{4c}$$

Here L_x and L_e are the fractions of the (e.g. triplet) excitation at time zero introduced in the X and E moieties, respectively. I_x and I_e are the total number of milliEinsteins of light effectively transferred to excitation in the two moieties while I is the total amount of light absorbed.

The total quantum yield in the presence of quencher is given by[26]

$$\phi =$$

$$\phi_{isc} \left[\frac{[(K_e + k_{qe}Q)L_x + k_2]k_{rx} + [(K_x + k_{qx}Q)L_e + k_1]k_{re}}{(K_x + k_1 + k_{qx}Q)(K_e + k_2 + k_{qe}Q) - k_1k_2} \right] \tag{5}$$

The unquenched efficiency is

$$\phi_0 = \phi_{isc} \left[\frac{[K_eL_x + k_2]k_{rx} + [K_xL_e + k_1]k_{re}}{(K_x + k_1)(K_e + k_2) - k_1k_2} \right] \tag{6}$$

Thus,

$$\phi_0/\phi = AB \tag{7a}$$

where

$$A = \left[1 + \frac{(k_{qe}k_{rx}L_x + k_{qx}k_{re}L_e)Q}{[K_eL_x + k_2]k_{rx} + [K_xL_e + k_1]k_{re}} \right]^{-1} \tag{7b}$$

$$B = \left[1 + \frac{[k_{qe}(K_x + k_1) + k_{qx}(K_e + k_2)]Q + k_{qe}k_{qx}Q^2}{k_1K_e + k_2K_x + K_eK_x} \right] \tag{7c}$$

The four observations noted above can be accounted for if we assume a rapid equilibrium of the two excited states X and E. Thus, $k_2 \gg K_e$ and $k_1 \gg K_X$; that is, the equilibration rates are taken as large compared with the total decay rates. These inequalities alone lead to $\phi_0/\phi = AB$ where A and B are now given in eq 8.

$$A = \left[1 + \frac{(k_{qe}k_{rx}L_x + k_{qx}k_{re}L_e)Q}{k_2k_{rx} + k_1k_{re}} \right]^{-1} \tag{8a}$$

$$B = \left[1 + \frac{[k_{qe}k_1 + k_{qx}k_2]Q + k_{qe}k_{qx}Q^2}{k_1K_e + k_2K_x} \right] \tag{8b}$$

However, we note that eq 8 in general describes a nonlinear Stern–Volmer plot. But, additional consequences of rapid equilibration lead us to a further simplification, one which accounts for the linearity of the Stern–Volmer treatment.

We might first ask what conditions might lead to the observed Stern–Volmer linearity. If $A = 1$ and if the Q^2 term in B disappears, we have a linear situation. Both situations occur when eq 9 are satisfied. Equations 9a and 9b hold when k_1/k_{rx}, k_2/k_{re},

$$(k_{qe}k_{rx}L_x + k_{qx}k_{re}L_e)Q < k_1k_{re} + k_2k_{rx} \tag{9a}$$

$$k_{qe}k_{qx}Q < k_{qe}k_1 + k_{qx}k_2 \tag{9b}$$

k_1/k_{qx}, and k_2/k_{qe} are large as would occur when k_1 and k_2 are large. We see that these conditions are inherent in the assumption of rapid energy transfer.

The aim of finding the requirements for linearity is to determine the nature of the Stern–Volmer slope and also the unquenched quantum yield itself. The conditions for linearity lead to eq 10.[26d,e]

$$\text{slope} = (k_q\tau)^{\text{empir}} = \frac{k_{qe}k_1 + k_{qx}k_2}{k_1K_e + k_2K_x} = \frac{(k_{qe}F_1\tau_e + k_{qx}F_2\tau_x)}{F_1 + F_2} \tag{10}$$

where

$$F_1 = k_1/K_x \text{ and } F_2 = k_2/K_e$$

(23) (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. *J. Am. Chem. Soc.* **1982**, *104*, 2928-2929.

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(25) (a) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 159-161. (b) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965-1973.

(26) (a) Kinetic expressions related to eq 5-7 have been reported for cases where one of two interconverting excited states may react. For the case of nonequilibration, note ref 20 and 26b. For an expression related to eq 8, note ref 26c. (b) Shetlar, M. J. *Mol. Photochem.* **1973**, *5*, 311. (c) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1974**, *96*, 3668-3670. (d) Lamola, A. A. *J. Am. Chem. Soc.* **1970**, *92*, 5045. (e) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474.

Scheme III. General Kinetic Outline
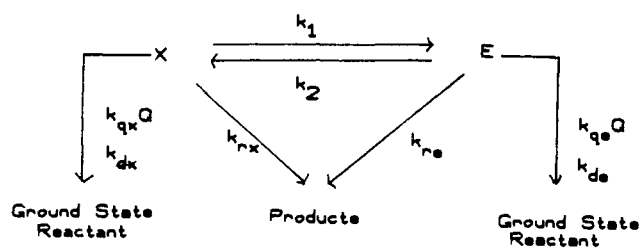
Here we note the situation encountered by Wagner and Nakahira,[26c] who described the first example of nonlinearity due to quenching of the energy transfer between one reactive chromophore and one nonreactive chromophore in the same system. We did not use high enough quencher concentrations for this complication to develop.

Next we turn to the quantum yield expressions. For rapid equilibrium, eq 6 leads to[26d,e]

$$\phi_0 = \phi_{isc}\left[\frac{F_1\phi_e + F_2\phi_x}{F_1 + F_2}\right] = \phi_{isc}\left[\frac{k_1\phi_e\tau_x + k_2\phi_x\tau_e}{k_1\tau_x + k_2\tau_e}\right] \quad (11)$$

where

$$F_1 = k_1/K_x \text{ and } F_2 = k_2/K_e$$

Equation 11 does predict a quantum yield independent of distribution of triplet excitation at time zero (i.e., independent of L_x and L_e). Conversely, it can be shown that for slow equilibration the quantum yield is not independent of initial site of excitation.

We now consider further application of the preceding kinetic analysis. Experimentally, as noted above, for the molecules now under study in direct irradiation runs localization of triplet excitation at intersystem crossing time zero is likely, but not certain, to be in the enone moiety in view of the rapid rate of intersystem crossing in enones as a consequence of spin–orbit coupling.

First let us discuss the observed $k_q\tau$ value as determined by Stern–Volmer methods. With a single chromophore and a single reacting excited state, one uses this value, along with the rate of diffusion as k_q, to determine $k_r = \phi/\tau$, the rate of excited-state reaction. With two potentially reactive excited states as in the present study, we turn to the results in eq 10.

It is seen in eq 10 that the τ value obtained experimentally corresponds to a linear combination of the two τ values characteristic of the individual excited states having excitation localized in one or the other of the two chromophores.[26d,e] τ_e and τ_x have weightings of $F_1/(F_1 + F_2)$ and $F_2/(F_1 + F_2)$. The F's are defined in connection with eq 10. Thus each F consists of the ratio of the rate of conversion to the alternative excited state divided by the total of the rates of reaction and radiationless decay.

For the special case, as for X being biphenylyl, where $k_1 = k_2$ due to the near isoenergetic triplet equilibration, eq 12 results.

$$\text{slope} = (k_q\tau)^{empir} = \frac{k_{qe} + k_{qx}}{K_e + K_x} = \frac{\tau_e\tau_x(k_{qe} + k_{qx})}{\tau_x + \tau_e} \quad (12)$$

Here the $k_q\tau$ values obtained can be seen to be a mean value of the individual lifetimes of the two chromophores,

Electronic Excitation and the Rearrangement. With the two chromophores being matched in energy, the question arises concerning which chromophore is actually reacting. In the direct irradiations, as noted, it seems likely that the excitation is initially localized in the enone end of the molecule. In contrast, on sensitization one might expect delivery of excitation to either or both ends of the molecule.

In conclusion, the behavior of this enone system is that understood best on the basis of a rapid triplet equilibration compared with the rate of rearrangement.

Molecular Rearrangement Mechansim. The overall mechanism is structurally quite similar to that proposed earlier[3,11] wherein the aryl group bridges to the β-carbon of the enone moiety.

Scheme IV. Mechanism of Enone Rearrangement
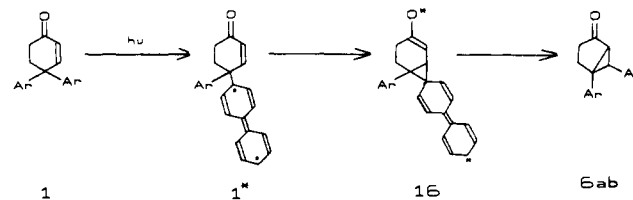
Scheme V. Possible Decay and Reaction Routes
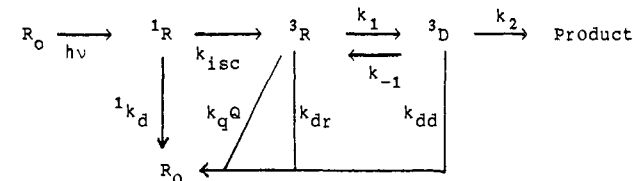
However, here we can envisage a competitive mechanism being available, namely a di-π-methane rearrangement involving the excited biphenylyl moiety and the α,β-enone π bond. Independent of which chromophore is initially excited, as bridging between the γ-aryl and the β-carbon occurs, excitation becomes delocalized, and the same bridged diradical is engendered. For such delocalized systems the π–π^* triplet is of lower energy than the n–π^* species and one would expect the bridged molecule to have the former configuration, independent of the nature of the initial excited state. This mechanism is depicted in Scheme IV,

An especially interesting observation is that the empirically observed triplet lifetimes of all of the 4,4-diarylcyclohexenones fall within a factor of 4 of one another independent of which chromophore is lower in energy and also independent of whether decay or reaction predominates. This point is discussed in some detail in our accompanying publication.[14a] However, the lifetimes do increase within this range as the 4-aryl group is changed from phenyl to biphenylyl to naphthyl. This seems to reflect the longer lifetime contributions from these groups in the linear combination. Still, the lifetimes observed for these 4,4-diarylcyclohexenones are short, of the order of nanoseconds, compared with the lifetimes of the chromophores as individual molecules. Hence the rapid decay must derive from cooperative interaction (e.g., incipient bridging) between the group and the enone. Finally, the primary factor controlling the rate of rearrangement seems to be the facility of aryl bridging to the β-carbon along with the probability of continuation on to product rather than reversion to reactant S_0.

The Consequence of Diradical Decay. Many photochemical rearrangements which proceed via a diradical species which provides a channel for decay to an S_0 hypersurface. One needs to consider the consequence in the significance of the measured rates of rearrangement and decay. Thus in Scheme V the reactant triplet (^3R) leads onward to a triplet diradical (^3D) which might be a species such as 16 in Scheme IV. This diradical has the possibility of decaying to ground-state reactant R_0, proceeding onward to product, or possibly reverting to excited-state reactant ^3R. Our early studies[3] suggest that the rate-limiting portion of the enone rearrangement is the bridging process so that the last may not be a necessary consideration.

It may be shown that in the general case eq 13 and eq 14 hold.

$$\tau(\text{measured}) = \frac{(k_2 + k_{-1} + k_{dd})}{(k_2 + k_{-1} + k_{dd})(k_1 + k_{dr}) - k_1k_{-1}} \quad (13)$$

$$k_r(\text{operational}) = (k_1k_2)/(k_2 + k_{-1} + k_{dd}) \quad (14)$$

Thus the measured lifetime is an operational value which becomes $(k_1 + k_{dr})$, or the usual τ, when k_{-1} vanishes which would result if, indeed, bridging is rate limiting. The operational rate constants obtained give us the ordinary rate constant for bridging (i.e., k_1) multiplied by the probability of the diradical proceeding onward to product (i.e., $k_2/(k_2 + k_{-1} + k_{dd})$).

Consequences of the Equienergy Chromophore. Table IV provides a comparison of the reactivity observed for the rear-

Photochemistry of a Biphenylyl-Substituted Cyclohexenone

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Table IV. Comparison of Diphenyl and Biphenylyl Enone Reactivity[a]

compound	ϕ	τ, ns	$k_{d(tot)}$, s^{-1}	k_r, s^{-1}
dibiphenylyl (1)	0.36	2.9	3.4×10^8	1.3×10^8
diphenyl[b] (3)	0.043	1.9	5.3×10^8	2.3×10^7

[a] Benzene solvent. [b] Recalculated values using current rates of diffusion to permit comparison.

rangement (i.e., k_r) for the dibiphenylyl enone triplet of **1** with the reactivity of the corresponding diphenyl enone analogue **3**. It can be seen that the rate of radiationless decay of the dibiphenylyl enone triplet is circa twofold slower than that of the diphenyl enone triplet. This may derive from energy storage in the long-lived biphenylyl triplet moiety. In addition, there is a fivefold greater rate of triplet rearrangement compared with the diphenyl case. This difference can be ascribed to the greater delocalization of odd electron density in the bridged species (note Scheme IV) where biphenylyl is the bridging aryl group. The diminished decay coupled with the enhanced rearrangement rate then accounts for the increase in quantum yield with biphenylyl substitution.

Conclusion. The photochemistry of the dibiphenylyl enone reveals that the classical aryl cyclohexenone rearrangement is not inhibited by the presence of a moiety which externally acts as a weak quencher but is instead enhanced. It appears that internal low-energy chromophores provide a means of storing energy. Also such extended π-system chromophores as biphenylyl increase reactivity in migrations. Finally, it is seen that the role of the relative energies of chromophores in photochemistry provides an additional dimension and controlling variable to organic photochemistry.

Experimental Section[27]

Dibiphenylyl-1-(1-hydroxy-1-cyclopentyl)carbinol. To a suspension of 10 g (42.9 mmol) of 4-bromobiphenyl in 40 mL of THF at −70 °C were added 30.0 mL (45.0 mmol) of 1.5 M *n*-butyllithium in hexane over 10 min. The green solution was allowed to warm for 10 min, after which it was recooled to −70 C, and a solution of 2.26 g (14.3 mmol) of ethyl 1-hydroxycyclopentanecarboxylate in 10 mL of THF was added dropwise. After being warmed to room temperature and stirred for 1 h, the reaction was quenched with 10 mL of water, and sufficient water was added to dissolve the inorganic salts. Neutral workup with ether yielded 9.42 g of a yellow oil, which was chromatographed on a 4 × 80 cm silica gel column. Elution with 1.5 L of hexane gave 1.4 g of biphenyl. Further elution with 10% ether–hexane gave 4.44 g (74%) of the desired diol. Recrystallization from chloroform–hexane yielded 2.37 g (40%) of dibiphenylyl-1-(1-hydroxy-1-cyclopentyl)carbinol, mp 112–114 °C. The spectral data were the following: IR (CHCl₃) 3580, 3050, 3020, 2995, 2955, 2865, 1600, 1560, 1487, 1445, 1400, 1340, 1320, 1300, 1210, 1165, 1075, 1040, 1005, 950, 918, 905, 840 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 7.1 (m, 18 H, arom), 2.82 (s, 1 H, OH), 2.2–1.2 (m, 8 H, four CH₂'s), 1.84 (s, 1 H, OH).

Anal. Calcd for C₃₀H₂₈O₂: C, 85.68; H, 6.71. Found: C, 85.62; H, 6.82.

2,2-Dibiphenylylcyclohexan-1-one. The procedure of Burger[29] for the 2,2-diphenyl analogue was modified. A solution of 10 g (23.8 mmol) of

dibiphenylyl-1-(1-hydroxy-1-cyclopentyl)carbinol in 30 mL of glacial acetic acid was heated just below reflux, and 40 mg (0.16 mmol) of iodine in 15 mL of acetic acid at the same temperature was added rapidly. After 5 min of reflux, the mixture was poured onto ice and sodium thiosulfate, the resulting solid being collected, water washed, and dissolved in benzene. Basic workup with ether afforded 9.1 g of yellow solid, which was recrystallized from methanol to yield 8.5 g (85%) of colorless crystals of 2,2-dibiphenylylcyclohexan-1-one, mp 185–187 °C. The spectral data were the following: IR (CHCl₃) 3020, 2945, 2868, 1712, 1603, 1490, 1543, 1270, 1130, 1080, 1013, 840, 720, 702 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 7.0–7.7 (m, 18 H, arom), 2.5 (m, 4 H, two CH₂'s), 1.8 (m, 4 H, two CH₂'s); MS, *m/e* 402.1984 (calcd for C₃₀H₂₆O, *m/e* 402.1984).

Anal. Calcd for C₃₀H₂₆O: C, 89.51; H, 6.51. Found: C, 89.31; H, 6.54.

2,2-Dibiphenylylcyclohexan-1-one Tosylhydrazone. The general procedure of Dauben and Shapiro[30,31] was modified to permit isolation of the tosylhydrazone. To 2.00 g (4.98 mmol) of 2,2-biphenylylcyclohexanone and 0.93 g (4.98 mmol) of *p*-toluenesulfonohydrazide in 10 mL of THF was added 0.10 mL of concentrated hydrochloric acid. The mixture was refluxed for 20 h, 20 mL benzene were added, and the solution was concentrated in vacuo to yield 2.70 g (95%) of a yellow oil which crystallized upon cooling to 0 °C. Recrystallization from ether–THF yielded 2.51 g (88%) of 2,2-dibiphenylylcyclohexanone tosylhydrazone, mp 229–231 °C dec. The spectral data were the following: IR (KBr) 3020, 3005, 2955, 2872, 1600, 1578, 1450, 1380, 1335, 1168, 1090, 1010, 916, 832 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 6.6–7.7 (m, 22 H, arom), 3.6 (s, 1 H, NH), 2.2–2.6 (m, 6 H, CH₂'s), 1.6 (s, 3 H, CH₃).

Anal. Calcd for C₃₇H₃₄N₂O₂S: C, 77.86; H, 6.00. Found: C, 77.69; H, 6.01.

3,3-Dibiphenylylcyclohex-1-ene. To a solution of 2.5 g (4.4 mmol) of 2,2-dibiphenylylcyclohexan-1-one tosylhydrazone in 20 mL of dry benzene cooled to 0 °C were added dropwise 18 mL (12.6 mmol) of 0.7 M methyllithium in ether. After being stirred at room temperature for 1 h, the reaction was quenched with 2.0 mL of water and poured into water. Neutral workup with methylene chloride afforded 1.56 g of crude product, which was recrystallized from chloroform–pentane to yield 1.38 g (82%) of pale yellow crystals, mp 191–192.5 °C. An analytical sample was obtained by sublimation at 165 °C, 0.5 torr, mp 198–199 °C. The spectral data were the following: IR (CHCl₃) 3080 (sh), 3056 (sh), 3020, 2940, 2865, 2839, 1600, 1482, 1448, 1400, 1122, 1076, 1008, 916, 836, 698 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 6.8–8.0 (m, 18 H, arom), 6.0–6.2 (d, 1 H, *J* = 10.5 Hz, =CH), 5.8–6.0 (dt, 1 H, *J* = 10.5, 3.0 Hz, =CH), 1.2–2.5 (m, 6 H, 3CH₂'s); MS, *m/e* 386.2034 (calcd for C₃₀H₂₆, *m/e* 386.2035).

Anal. Calcd for C₃₀H₂₆: C, 93.22; H, 6.78. Found: C, 93.37; H, 6.84.

4,4-Dibiphenylylcyclohex-2-en-1-one. The Dauben reaction[32] was used with modification. To the complex of 7.92 g (100 mmol) of dry pyridine and 5.00 g (50 mmol) of chromium trioxide in 110 mL of dry methylene chloride was added a solution of 1.00 g (2.5 mmol) of 3,3-dibiphenylylcyclohex-1-ene in 10 mL of dry methylene chloride. After being stirred for 48 h at room temperature, the mixture was filtered, and the resulting solid was washed with ether. The combined organic phase was washed with 5% sodium hydroxide, and acidic–basic workup with ether afforded 1.03 g of yellow solid which was chromatographed on a 2.5 × 75 cm silica gel column. Elution was done with 1.1 L hexane, 500 mL of 5% ether–hexane, and 900 mL 10% ether–hexane, and 100 mL fractions were collected to give fractions 5–8 (0.42 g of 3,3-diphenylylcyclohex-1-ene) and 19–25 (0.51 g (49%) of dibiphenylyl enone, mp 148–150 °C). Recrystallization from 95% ethanol yielded 0.38 g (37%) of 4,4-dibiphenylylcyclohex-2-en-1-one, mp 149.5–151 °C. The spectra data were the following: IR (CHCl₃) 3075 (sh), 3052 (sh), 3006, 2952, 2922, 2866, 2854, 1675, 1600, 1483, 1450, 1073, 1003, 928, 890, 830, 690 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 7.7–6.9 (m, 19 H, arom and β =CH), 6.2 (d, 1 H, *J* = 10 Hz, α CH=), 2.1–2.8 (m, 4 H, CH₂'s); MS, *m/e* 400.1828 (calcd for C₃₀H₂₄O, *m/e* 400.1827); UV (cyclohexane) λ (max) 256 (ε 42336), 325 (ε 153), 350 nm (ε 42), 366 (ε 8), 378 nm (ε <0.1).

Anal. Calcd for C₃₀H₂₄O: C, 89.96; H, 6.04. Found: C, 89.77; H, 6.10.

Lithium–Liquid Ammonia Reduction of *trans*-5,6-Dibiphenylylbicyclo[3.1.0]hexan-2-one. To a solution of 201 mg (0.50 mmol) of *trans*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one in 30 mL of anhydrous

(27) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratory, Inc., Knoxville, TN. All reactions were run under a dry nitrogen atmosphere with distilled solvents. THF was purified by storage over KOH, followed by successive distillation from calcium hydride, lithium aluminum hydride, and sodium/ benzophenone ketyl. Column chromatography was performed with silica gel (Davison Chemical Co., Davisil 62, 60–200 mesh) or Florisil (Fisher Scientific Co., 60–100 mesh) mixed with Sylvania 2282 phosphor and slurry-packed into quartz columns, allowing monitoring with a hand-held UV lamp. Neutral workup refers to dilution with the indicated solvent, successive washing with water and brine, drying over anhydrous magnesium sulfate, filtration, and concentration in vacuo. Basic workup added an initial saturated aqueous sodium bicarbonate wash after dilution. Acidic–basic workup used a 5% aqueous hydrochloric acid wash prior to the base wash. Workup A for lithium–liquid ammonia reductions refers to quenching with ammonium chloride, evaporation of the liquid ammonia, ether extraction of the residue, drying over magnesium sulfate, and concentration in vacuo. Oxygen-free nitrogen, when needed, was purified by the method of Meites.[28]

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ether and 60 mL of freshly distilled ammonia at −78 °C were added 7.0 mg (1.00 g-atom) of freshly cut lithium metal. The dark blue color developed and then disappeared within 5 min. Standard workup A with ether afforded 203 mg of crude product, which was recrystallized from 95% ethanol to yield 125 mg (61%) of cis-3,4-dibiphenylylcyclohexanone, mp 155–156 °C. The spectral data were the following: IR (KBr) 3040, 3020, 2930, 2860, 1705, 1600, 1487, 1450, 1410, 1328, 1226, 1195, 1150, 1070, 1009, 965, 850, 770, 750, 700 cm^{-1}; NMR (CDCl$_3$, 100 MHz) δ 7.50–6.68 (m, 18 H, aromatic), 3.70 (m, 1 H, J_{max} = 4 Hz, CH), 3.60 (dt, 1 H, J = 12.5, 3.5 Hz, CH), 3.04–2.66 (m, 4 H, CH$_2$'s α to carbonyl), 2.35 (m, 1 H, CH$_2$), 2.32 (m, 1 H, CH$_2$); MS, m/e 402.1984 (calcd for C$_{30}$H$_{24}$O, m/e 402.1984).

Anal. Calcd for C$_{30}$H$_{24}$O: C, 89.51; H, 6.51. Found: C, 87.40; H, 6.71.

Lithium–Liquid Ammonia Reduction of cis-5,6-Dibiphenylylbicyclo-[3.1.0]hexan-2-one. A solution of 377 mg (0.943 mmol) of cis-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one in 50 mL of THF was added to a solution of 38 mg (5.5 g-atom) of freshly cut lithium in 150 mL of freshly distilled ammonia. After 20 min the muddy brown mixture was quenched by addition of solid sodium benzoate, and standard workup A afforded 347 mg of a white solid, mp 53–64 °C. HPLC analysis indicated one major product and four minor products. Chromatography on a 3.2 × 53 cm silica gel column eluted with 10–20% ether–hexane gave 79 mg of a mixture of four compounds not further characterized, followed by 209 mg (56%) of crude 2-(biphenylmethyl)-3-biphenylylcyclopentanone, mp 91–96 °C. Recrystallization from ether yielded 55.7 mg (15%) of analytically pure material, mp 93–97 °C. The spectral data were the following: IR (CHCl$_3$) 3040, 3020, 3000, 2930, 2860, 1736, 1600, 1525, 1490, 1450, 1410, 1345, 1285, 1150, 1115, 1080, 1010, 845 cm^{-1}; NMR (CDCl$_3$, 100 MHz) δ 7.53–7.07 (m, 18 H, arom), 3.09 (dd, 1 H, J = 13.9, 5.1 Hz, benzylic CH$_2$), 2.99 (m, 1 H, benzylic CH$_2$), 2.71 (m, 1 H), 2.53 (m, 1 H), 2.30–2.06 (m, 2 H), 1.96–1.84 (m, 1 H); MS, m/e 402.1984 (calcd for C$_{30}$H$_{26}$O, m/e 402.1984).

Anal. Calcd for C$_{30}$H$_{26}$O: C, 89.51; H, 6.51. Found: C, 89.69; H, 6.75.

3,4-Dibiphenylylcyclohex-2-en-1-one. A suspension of 1.00 g (2.88 mmol) of 1,2-dibiphenylyl-2-ethanone[33] in 90 mL of THF was cooled to −10 °C, and 288 µL of 3 N ethanolic potassium hydroxide were added over 10 min. The yellow solution was stirred for 10 min, and 232 µL of methyl vinyl ketone were then added over 15 min, the solid dissolving after 180 µL had been added. The mixture was stirred at room temperature for 2 h, refluxed for 2 days, and then poured onto ice and 1 N hydrochloric acid with stirring. Neutral workup with methylene chloride yielded crude product, which was chromatographed on a 3 × 45 cm silica gel column. Elution was done with 20% ether–hexane, and 500-mL fractions were collected to give fractions 6–10 (935 mg of 3,4-dibiphenylylcyclohex-2-en-1-one, mp 72–80 °C). The material was further purified by preparative silica gel TLC. Eight 20 × 20 cm plates were each eluted three times with 10% ethyl acetate–hexane to give two poorly-resolved bands. The combined top fractions yielded 550 mg of pure material, mp 128–131 °C. The combined bottom fractions yielded 270 mg of impure material, mp 65–84 °C, which was again subjected to preparative TLC to yield an additional 86 mg, mp 128–131 °C. The combined material was recrystallized from 95% ethanol to give 283 mg (25%) of pure 3,4-dibiphenylylcyclohex-2-en-1-one, mp 128–131 °C. The spectral data were the following: IR (KBr) 3080, 3040, 3020, 2930, 1665, 1600, 1555, 1520, 1490, 1450, 1410, 1345, 1302, 1260, 1200, 1172, 1150, 1120, 1080, 1010, 1000, 985, 975, 920, 890, 852, 840, 770, 750, 740, 695 cm^{-1}; NMR (CDCl$_3$, 100 MHz) δ 7.70–7.25 (m, 1, H, arom), 6.64 (s, 1 H, CH=C), 4.25 (m, 1 H, CH), 2.40 (m, 4 H, CH$_2$'s); MS, m/e 400.1828 (calcd for C$_{30}$H$_{24}$O, m/e 400.1827).

Anal. Calcd for C$_{30}$H$_{24}$O: C, 89.97; H, 6.04. Found: C, 89.87; H, 6.12.

cis-3,4-Dibiphenylylcyclohexan-1-one. To 200 mL of freshly distilled ammonia at −78 °C were added 43 mg (6.22 g-atom) of freshly cut lithium. A solution of 0.50 g (1.24 mmol) of the 3,4-dibiphenylyl enone in 40 mL of THF was added all at once, and after 8 min the blue solution became yellow. Standard workup A with chloroform afforded a 1:1 mixture (NMR) of product and starting material. The reduction procedure was repeated on this material to give a 3:1 mixture of product and starting material. Chromatography on a 2 × 200 cm silica gel column eluting with 7.5% ether–hexane and collecting 40-mL fractions gave fractions 141–175 (120 mg of cis-3,4-dibiphenylylcyclohexanone) and 176–185 (122 mg of a mixture of starting material and product). HPLC purification of the latter fractions with 10% ethyl acetate–hexane and 10–15 µm spherical silica gave 40 mg of product and 55 mg of reactant. Recrystallization of the combined product from 95% ethanol yielded 160 mg (32%) of cis-3,4-dibiphenylylcyclohexanone, mp 156–158 °C. The

spectral data were identical with those of the compound obtained in the lithium–liquid ammonia reduction of trans-5,6-dibiphenylylbicyclo-[3.1.0]hexan-2-one.

3-Biphenyl-2-(phenylthio)cyclopentanone. To a solution of 24.13 g (103.4 mmol) of 4-bromobiphenyl in 340 mL of ether at 0 °C were added 68.8 mL (103.2 mmol) of 1.5 M n-butyllithium in hexane. After the solution was stirred for 10 min and cooled to −78 °C, 20.3 g (12.9 mmol) of tetrakis(tri-n-butylphosphine)copper(I) iodide[34] in 180 mL of ether at −78 °C were added over 40 min. After being stirred for 30 min, a solution of 2.46 g (12.9 mmol) of 2-(phenylthio)cyclopent-2-en-1-one[35] in 80 mL of ether was added over 30 min. The reaction was stirred for 1.5 h at −78 °C, warmed to −20 °C, and quenched by adding 100 mL of saturated aqueous ammonium chloride. After being warmed to 10 °C, the organic layer was decanted, and the residual aqueous solids were diluted with ammonium chloride. Neutral workup with ether yielded crude product, which was chromatographed on a 3 × 50 cm Florisil column. Elution with 1 L of hexane gave 15.3 g of impure biphenyl, and further elution with 10–80% ether–hexane gave 4.45 g of a mixture of 3-biphenylyl-2-(phenylthio)cyclopentanone and tri-n-butylphosphine, mp 67–75 °C. Recrystallization from ether yielded 3.65 g (82%) of cubic crystals of the cyclopentanone, mp 88–89 °C. The spectral data were the following: IR (KBr) 3080, 3020, 2970, 2930, 2890, 1744, 1600, 1585, 1570, 1490, 1470, 1440, 1410, 1310, 1285, 1225, 1205, 1195, 1170, 1135, 1120, 1085, 1070, 1030, 1010, 980, 930, 840, 770, 740, 700 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 7.62–7.19 (m, 14 H, arom), 3.58 (d, 1 H, J = 10.3 Hz, CHSAr), 3.23 (ddd, 1 H, J = 10.5, 10.3, 6.4 Hz, CHAr), 2.57 (m, 1 H, α CH$_2$), 2.42 (m, 1 H, β CH$_2$), 2.26 (m, 1 H, α CH$_2$), 2.03 (m, 1 H, β CH$_2$); MS, m/e 344.1234 (calcd for C$_{23}$H$_{20}$SO, m/e 344.1235).

Anal. Calcd for C$_{23}$H$_{20}$SO: C, 80.20; H, 5.85. Found: C, 80.09; H, 6.00.

3-Biphenylyl-2-(biphenylylmethyl)-2-(phenylthio)cyclopentanone. To 200 mg (1.11 mmol) of 22.2% potassium hydride in mineral oil suspended in 3.0 mL of DME at 0 °C was added a solution of 300 mg (0.87 mmol) of 3-biphenylyl-2-(phenylthio)cyclopentanone in 3.0 mL of DME. Hydrogen evolution was observed for 3 min, but only after 6 µL (0.106 mmol) of ethanol were added. A solution of 342 mg (1.38 mmol) of p-phenylbenzyl bromide in 3.0 mL of DME was added, and the reaction was stirred for 2 h at 0 °C and for 19 h at room temperature. After the mixture was cooled to 0 °C and quenched with saturated ammonium chloride, neutral workup with chloroform yielded crude product, which was chromatographed on a 1.2 × 40 cm Florisil column. Elution was done with 3–5% ether–hexane, and 500-mL fractions were collected to give fractions 10–14 (304 mg of impure 3-biphenyl-2-(biphenylmethyl)-2-(phenylthio)cyclopentanone, mp 87–93 °C). Further purification by preparative HPLC (8% ethyl acetate in hexane) gave 61.8 mg of a compound not further characterized, mp 114–119 °C, followed by 211 mg (48%) of the desired product, mp 177–180 °C. Recyrstallization from ether gave 164 mg (37%) of analytical material, mp 191–193 °C. The spectral data were the following: IR (KBr) 3040, 3020, 2940, 1728, 1600, 1580, 1520, 1487, 1475, 1450, 1440, 1410, 1285, 1230, 1180, 1145, 1120, 1080, 1030, 1020, 1010, 975, 920, 880, 845, 775, 760, 750, 700 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 7.67–7.19 (m, 23 H, arom), 3.51 (t, 1 H, J = 7.1 Hz, CHAr), 3.43 (d, 1 H, J = 14.3 Hz, CH$_2$Ar), 3.04 (d, 1 H, J = 14.3 Hz, CH$_2$Ar), 2.88 (m, 1 H), 2.60 (m, 1 H), 2.17 (m, 2 H); MS, m/e 510.2018 (calcd for C$_{36}$H$_{30}$SO, m/e 510.2017).

Anal. Calcd for C$_{31}$H$_{30}$SO: C, 84.67; H, 5.92. Found: C, 84.48; H, 6.01.

2-(Biphenylylmethyl)-3-biphenylylcyclopentanone. The desulfurization method of Trost[36] was modified. To a solution of 100.4 mg (0.197 mmol) of 3-(biphenylylmethyl)-2-biphenylyl-2-(phenylthio)cyclopentanone in 10 mL of THF was added a suspension of 110 mg (0.775 mmol) of disodium hydrogen phosphate in 5.0 mL of methanol and 300 mg (0.783 mmol) of 6% sodium amalgam. After the solution was stirred overnight and separation of the organic layer from the mercury droplet, 20 mL of water were added, and neutral workup with ether including a 5% sodium hydroxide wash yielded 82.8 mg of an oily solid. Purification by HPLC (25% ethyl acetate in hexane) gave 65.1 mg (82%) of 2-(biphenylyl-methyl)-3-biphenylylcyclopentanone, mp 96–98 °C. The spectra data were identical with those of the compound obtained in the lithium–liquid ammonia reduction of trans-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one.

General Procedure for Exploratory Irradiations. All exploratory irradiations were performed with a 450-W medium-pressure mercury lamp in an immersion apparatus fitted with a Pyrex filter sleeve. Solutions

(33) Gomberg, M.; Van Natta, F. T. *J. Am. Chem. Soc.* **1929**, *51*, 2238–2245.

(34) Kirschner, S. *Inorg. Synth.* **1960**, *6*, 3–6.

(35) Monteiro, H. *J. Org. Chem.* **1977**, *42*, 2324–2326.

(36) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, P. R. *Tetrahedron Lett.* **1976**, 3477–3478.

(37) (a) Spherical silica bead packings were prepared by emulsion polymerization[37b] and generally had 3000–6000 plates per 25 cm. (b) Zimmerman, H. E., to be published.

Table V. Summary of Quantum Yield Runs[a]

run	light, mEinstein	additive	conversion, %	trans [3.1.0] mg	cis [3.1.0] mg	3,4-enone mg	ϕ trans	ϕ cis	ϕ 3, 4
1D	0.0930		8.2	6.03	0.24	0.29	0.16	0.006	0.008
2D	0.0591		6.4	4.68	0.20	0.24	0.20	0.008	0.010
3D	0.0451		5.1	3.68	0.16	0.22	0.20	0.009	0.012
4D	0.0350		4.1	2.93	0.18	0.18	0.21	0.013	0.013
5D	0.0187		2.5	1.72	0.14	0.15	0.23	0.018	0.019
6D	0.0117		1.6	1.09	0.080	0.11	0.23	0.018	0.023
7D	0.00358		0.55	0.29	0.034	0.079	0.20	0.024	
8D	0.00108		0.11	0.092			0.21		
9D	0.0166		3.27	1.33	0.064	0.14	0.20	0.010	0.021
10D	0.0225		4.64	1.54	0.087	0.21	0.17	0.010	0.023
1S	0.0618	xanthone[b]	6.0	4.36	0.19	0.25	0.18	0.008	0.010
2S	0.0452	xanthone	4.9	3.53	0.18	0.21	0.20	0.010	0.012
3S	0.0346	xanthone	3.9	2.81	0.15	0.16	0.20	0.011	0.011
4S	0.0175	xanthone	2.2	1.48	0.13	0.15	0.21	0.019	0.020
5S	0.0496	benzophenone[c]	5.3	3.84	0.19	0.22	0.19	0.010	0.012
6S	0.0509	benzophenone	5.5	3.97	0.20	0.23	0.20	0.010	0.011
7S	0.0337	benzophenone	3.8	2.75	0.15	0.18	0.20	0.011	0.013
8S	0.0212	benzophenone	2.7	1.80	0.14	0.16	0.22	0.017	0.019
9S	0.0158	benzophenone	2.0	1.39	0.09	0.12	0.22	0.015	0.019
10S	0.0849	thioxanthone[d]	2.9	1.99	0.15	0.18	0.059	0.004	0.005
11S	0.0794	thioxanthone	2.8	1.91	0.15	0.17	0.060	0.005	0.005

[a] In each run 80.0 mg in 40 mL of solvent (0.0050 M) of 4,4-dibiphenylyl enone was photolyzed. [b] Runs 1D through 6D and 1S through 11S were run at 325 nm in *t*-BuOH. Runs 7D-10D were run at 280 nm in *tert*-butyl alcohol. Runs 1S-4S were 0.015 M in xanthone and photolyzed at 366 nm. [c] Run 5S was run with 0.20 M benzophenone at 350 nm and 6S-9S were run with 0.10 M benzophenone at 350 nm. [d] Runs 10S and 11S were at 0.010 M thioxanthone and run at 378 nm.

Table VI. Summary of Quenching Runs

run[a]	light mEinstein	concn quencher	conversion	quantum yield trans	ϕ_0/ϕ
1a	0.0402	0.000	6.75	0.28	1.00
2a	0.0401	0.040	4.85	0.23	1.24
3a	0.0406	0.080	3.75	0.19	1.47
4a	0.0405	0.120	3.25	0.16	1.75
5b	0.0259	0.000	4.20	0.33	1.00
6b	0.0253	0.040	2.20	0.19	1.77
7b	0.0253	0.080	1.70	0.13	2.46
8b	0.0368	0.120	1.96	0.10	3.10

[a] The "a runs" were in *tert*-butyl alcohol and the "b runs" were in benzene. Each run employed 80.0 mg of enone in 40.0 mL of solvent at 0.005 M.

were purged with purified nitrogen[28] for 1 h before and during the photolysis. *tert*-Butyl alcohol for photolysis was distilled from calcium hydride. Benzene for photolysis was repeatedly washed with acidic saturated aqueous potassium permanganate, followed by repeated washings with concentrated sulfuric acid, water, and brine, drying over magnesium sulfate, and distillation from calcium hydride.

Exploratory Photolysis of 4,4-Dibiphenylylcyclohex-2-en-1-one. With use of the general photolysis procedure, 810 mg (2.025 mmol) of 4,4-dibiphenylylcyclohex-2-en-1-one in 1 L of *tert*-butyl alcohol were irradiated for 40 min. Concentration in vacuo, followed by chromatography on a 2.5 × 95 cm silica gel column eluting with 5–30% ether-hexane, and collecting 100-mL fractions gave fractions 8–13 (36 mg of a solid not further characterized) 19–26 (651 mg (80%) of *trans*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one), 28–29 (75 mg (9%) of reactant enone), and 30–31 (48 mg (5%) of a mixture of *cis*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one and 3,4-dibiphenylylcyclohex-2-en-1-one).

A 110-mg sample of the final fraction mixture was subjected to silica gel chromatography to afford 55 mg of cis-bicyclic product and 46 mg of the 3,4-dibiphenylyl enone.

With use of the same procedure, 790 mg (1.98 mmol) of 4,4-dibiphenylyl enone in 700 mL of benzene were irradiated for 85 min, followed by concentration in vacuo. Silica gel chromatography and 95% ethanol recrystallization yielded 546 mg (70%) of trans-bicyclic product, mp 178.5-179.5 °C, and 158 mg (20%) of cis-bicyclic product, mp

209–210 °C. The spectra data for *trans*-5,6-dibiphenylylbicyclo-[3.1.0]hexan-2-one were the following: IR (CHCl₃) 3050, 2940, 2940, 2880, 1715, 1605, 1525, 1495, 1463, 1452, 1415, 1325, 1305, 1180, 1150, 1120, 1080, 1060, 1050, 1030, 1015, 1002, 950, 920, 895, 870, 850, 800, 705 cm⁻¹; NMR (CDCl₃, 270 MHz) δ 7.35-7.71 (m, 18 H, arom), 3.12 (ab, 1 H, *J* = 10.1 Hz, cyclopropyl), 2.68 (ab, 1 H, *J* = 10.1 Hz, cyclopropyl), 2.04 (t, 2 H), 1.72 (m, 1 H), 1.30 (m, 1 H); MS, *m/e* 400.1828 (calcd for C₃₀H₂₆O, *m/e* 400.1827).

Anal. Calcd for C₃₀H₂₆O: C, 89.97; H, 6.04. Found: C, 90.06; H, 6.05.

The spectral data for *cis*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one were the following: IR (CHCl₃) 3100, 3000, 1720, 1600, 1487, 1350, 1315, 1295, 1170, 1087, 1075, 1060, 1008, 990, 842, 700 cm⁻¹; NMR (CDCl₃, 270 MHz) δ 7.08-7.65 (m, 17 H, arom), 6.85 (m, 1 H, arom), 2.86 (ab, 1 H, *J* = 4.3 Hz, cyclopropyl), 2.68 (ab, 1 H, *J* = 4.3 Hz, cyclopropyl), 2.48 (m, 4 H, cyclopentyl); MS, *m/e* 400.1828 (calcd for C₃₀H₂₆O, *m/e* 400.1827).

Anal. Calcd for C₃₀H₂₄O: C, 89.97; H, 6.04. Found: C, 89.96; H, 6.18.

The spectral data of 3,4-dibiphenylylcyclohex-2-en-1-one were identical with that of synthesized material (vide infra).

Exploratory Photolysis of *trans*-5,6-Dibiphenylylbicyclo[3.1.0]hexan-2-one. With use of the general photolysis procedure, 88.3 mg (1.99 mmol) of *trans*-5,6-dibiphenylylbicyclo[3.1.0]hexan-2-one in 200 mL of benzene were irradiated for 1.25 h, followed by concentration in vacuo to afford 90.6 mg of a clear oil. HPLC analysis showed that the major photoproduct was the isomeric cis-bicyclo ketone **7b**, with minor amounts of 3,4-dibiphenylylcyclohex-2-en-1-one also present. Separation was achieved with preparative silica gel TLC with use of a 20 × 20 cm plate eluted with 10% ethyl acetate–hexane. The first-eluted band contained 62.4 mg of trans-bicyclic starting material, mp 175–178 °C, and the second-eluted band contained 24.5 mg of cis-bicyclic photoproduct, mp 208–210 °C. The spectral data were identical with those reported above.

Exploratory Photolysis of *cis*-5,6-Dibiphenylbicyclo[3.1.0]hexan-2-one. With use of the general photolysis procedure, 78.0 mg (0.195 mmol) of *cis*-bicyclohexanone in 200 mL of benzene were irradiated for 1.25 h, followed by concentration in vacuo to yield 75.9 mg of a white solid. HPLC analysis showed that the major product was the trans-bicyclo ketone, with lesser amounts of both the 3,4- and 4,4-dibiphenylylcyclohex-2-en-1-ones also present. Separation was achieved by using preparative silica gel TLC with 20 × 20 cm plates eluted with 10% ethyl acetate–hexane. The first-eluted band contained 48.0 mg of trans-bicyclo ketone, mp 174–177 °C, and the second-eluted band contained 22.1 mg of cis-bicyclo ketone starting material, mp 208–211 °C.

HPLC Analytical Methods. Analyses were performed with use of 0.3 cm × 25 cm columns packed with 5 μm spherical silica.[37] A 5000-psi (LDC) minipump equipped with pulse damper was used, and eluent UV absorbance was monitored with modified LDC and ISCO scanners.

(38) (a) PDP-11 programming afforded relative peak areas conveniently.[38b] (b) Zimmerman, H. E.; Moore, J.; Swafford, R. L., to be published.

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

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

(41) Hatchard, C. G.; Parker, C. W. *Proc. R. Soc. London, Ser. A* **1966**, *235*, 518–536.

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

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

Quenching Runs. These were run as in the direct photolyses, with cyclohexadiene present as the triplet quencher. These runs are summarized in Table VI.

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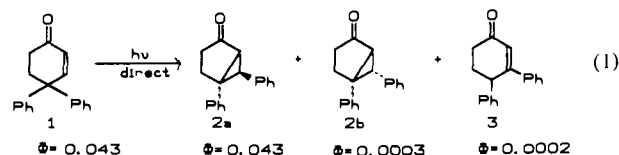
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Abstract: The photochemistry of 4,4-di(α-naphthyl)cyclohexenone and 4,4-di(β-naphthyl)cyclohexenone was investigated in order to ascertain the effect of having internally bonded moieties which, as external chromophores, would ordinarily serve as triplet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

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

and on dependence of efficiency and excited state rate on structure.[7] Most recently, however, we turned our attention to the

$$\Phi = 0.043 \qquad \Phi = 0.043 \qquad \Phi = 0.0003 \qquad \Phi = 0.0002$$

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

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

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

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