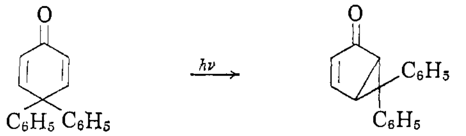
Mechanistic Organic Photochemistry. XXI.[1] Electronic Details of the 2,5-Cyclohexadienone Rearrangement

Howard E. Zimmerman and John S. Swenton[2]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received September 24, 1966*

Abstract: The rearrangement of 4,4-diphenylcyclohexadienone to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was shown to be an efficient process with a quantum yield of 0.85. The quantum efficiency was solvent independent. Evidence was obtained that the dienone triplet is involved. The triplet, formed by efficient intersystem crossing, rearranges at a rate greater than 2×10^{10} sec^{-1}. Additional results showed that after skeletal change the triplet demotes to a ground-state intermediate which then rearranges further to product; the ground-state intermediate is reasonably formulated as the mesoionic species postulated earlier. The excited triplet of bicyclic ketone product is not reached. The observed preference of the mesoionic zwitterion to proceed to bicyclic ketone rather than revert to dienone is understood on a molecular orbital basis. The *a priori* possible $4 \rightarrow 3$ phenyl migration was shown not to intervene. The dienone rearrangement did not occur at 77°K in a glass under conditions where the dienone triplet was quenched by naphthalene. Spectroscopic evidence showed the presence of the n-π^* triplet, and molecular orbital considerations suggest that this is the species rearranging. Naphthalene in high concentration was used as a singlet sensitizer.

Originally we reported[3] the gross features of the photochemical rearrangement of 4,4-diphenylcyclohexadienone (**1**) to afford 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**). In a preliminary communication,[4] we presented evidence bearing on selected aspects of the electronic details of the reaction. We now describe these results in full and report further findings allowing delineation of the reaction mechanism.



1 **2** (1)

The Reaction Efficiency. The quantum yield of the reaction was of interest for two reasons. First, we have been interested in correlating photochemical reaction efficiencies with available electronic pathways in order to ascertain the factors controlling the course of excited-state transformations. Secondly, the quantum yield was needed for comparison with sensitized efficiencies.

The quantum yield was determined in two ways. This was necessary since the bicyclic ketone product **2** was much more strongly absorbing than the dienone reactant **1**, with the result that with increasing time of irradiation diminishing fractions of the light were captured by the dienone.[5a] The first method was least-squares extrapolation of the apparent quantum yield to zero conversion. The extrapolated value for dienone disappearance was 0.81 while that for bicyclic ketone appearance was 0.85 mmole/mEinstein. The second method was designed to take into account light-absorbed by-product. Here the quantum yield was taken as

$$\phi = (D_0 - D)/(tI) + F/(tI) \qquad (2)$$

where

$$F = (\epsilon_p/\epsilon_d)[2.303D_0 \log (D_0/D) - (D_0 - D)] \qquad (3)$$

and t is the irradiation time, D is millimoles of dienone, I is the incident light in mEinsteins/hr, ϵ_p is the extinction coefficient of the product bicyclic ketone **2**, and ϵ_d is the extinction coefficient of the reactant dienone.[5b] Here we may interpret F as the decrease in amount of dienone reacted due to light absorption by product. In this second method $(D_0 - D)$ was obtained both from dienone disappearance and by equating this to bicyclic ketone appearance. The zero-time quantum yields obtained were 0.85 and 0.90, respectively. The average value of 0.85 ± 0.09 was then taken as the quantum yield in the 75% aqueous dioxane solvent employed. This efficient conversion seems typical of dienones. For example, the santonin to lumisantonin transformation has been reported by Richards[7] to be facile.

Multiplicity of the Reaction. Quantum yields for acetophenone-sensitized runs were determined in 75% aqueous dioxane and also in benzene containing 3% methanol. The concentrations were adjusted so that acetophenone absorbed more than 98% of the light. Also the dienone concentration was kept sufficiently low to ensure unimolecular destruction of acetophenone excited singlet molecules prior to collision with ground-state dienone molecules, yet sufficiently high to guarantee collision of acetophenone triplets with dienone faster than acetophenone decay.[8]

---

[1] For paper XVI of the series, note H. E. Zimmerman, R. Keese, J. Nasielski, and J. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).

[2] NSF Fellow, University of Wisconsin, 1963–1966.

[3] (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4484 (1961); (b) *ibid.*, **84**, 4527 (1962).

[4] H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 947 (1964).

[5] (a) Quantum yields when given should be accompanied by a statement that correction has been made for light capture by product or developing impurities, since this seems to be a major impediment in obtaining valid efficiencies. (b) Equations 2 and 3 were used in paper XII of the series.[6] However, in the present instance the treatment is imperfect in that bicyclic ketone **2** reacts further and thus is not given by $(D_0 - D)$. Were the treatment perfectly applicable, there would be no need for extrapolation to zero time.

[6] H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Am. Chem. Soc.*, **87**, 1138 (1965).

[7] M. H. Fisch and J. H. Richards, *ibid.*, **85**, 3029 (1963). These authors report the reaction to proceed with near unit efficiency although an exact number is not given for the quantum yield.

[8] Dienone concentrations of the order of 5–10 × 10^{-3} *M* were used. Assuming singlet energy transfer to be diffusion controlled with a rate constant of the order of 10^9 l. mole^{-1} sec^{-1} (*cf.* ref 9 for a summary of

The results of these runs, collected in Table I, show the average quantum yield for disappearance of dienone with acetophenone sensitization in aqueous dioxane to be 0.84 ± 0.08. The quantum yield for appearance of bicyclic ketone is 0.78 ± 0.08. The sensitized quantum yields in 97% methanolic benzene are comparable although perhaps slightly lower. The variation, which is small, may be due to experimental error.

Table I. Direct, Sensitized, and Quenched Quantum Yields of Conversion of 4,4-Diphenylcyclohexadienone to 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one

Solvent	Additive	Quantum yield[a]
75% aqueous dioxane	None	0.85 ± 0.09[b]
75% aqueous dioxane	Acetophenone[c]	0.81 ± 0.08[d]
97% methanolic benzene	Acetophenone[c]	0.77 ± 0.08[e]
75% aqueous dioxane	Naphthalene (0.10 *M*)[f]	0.75 ± 0.08[g]
75% aqueous dioxane	Naphthalene (0.05 *M*)[f]	0.81 ± 0.08[g]
Piperylene	. . .	0.16 ± 0.04[h]

[a] All runs at 25.0 ± 0.01°. [b] Extrapolated value (see text). [c] Absorbing over 98% of incident light. [d] Average of dienone disappearance and bicyclic ketone quantum yields for four runs. [e] Average of disappearance and appearance values for two shortest conversion runs. [f] Absorbing negligible light. [g] Disappearance value. [h] Disappearance value; no bicyclic ketone detected.

The observation that the same products were obtained in the sensitized photolyses as in the direct irradiations provides proof that the triplet of dienone can rearrange to bicyclic ketone **2**. The similarity of the direct run quantum yields with the sensitized ones provides strong suggestive evidence that it is the triplet which is responsible for the rearrangement in the direct runs as well.[11] It would be fortuitous but not impossible for the two excited states of different multiplicity, singlet, and triplet, to proceed onward to bicyclic ketone product with the same efficiency. A further conclusion based on this reasoning is that the intersystem crossing efficiency of dienone excited singlet to triplet is about unity. Whatever slightly inefficient steps detract from the quantum yield to bring it down to 0.85 must come after intersystem crossing.

To provide complementary evidence on the presence of a triplet, quenching was investigated. It was found (note Table I) that 0.05 and 0.10 *M* naphthalene produced no diminution of the quantum yield beyond experimental error.[12] If we make the conservative assumption that 20% quenching would have been observed (*i.e.*, $\phi_0/\phi_q < 1.2$) with 0.1 *M* naphthalene and then make the resonable assumption that quenching of dienone triplet will be diffusion controlled[13] with a bimolecular rate of diffusion of *ca.* 10^9 l. mole^{-1} sec^{-1},[8] and taking $k_r/(k_r + k_d) = \phi$ as 0.85, we can obtain a lower limit for the rate of rearrangement of dienone triplet by using eq 4

$$\phi_q/\phi_0 = [k_r + k_d]/[k_r + k_d + k_q(\mathrm{Q})] \qquad (4)$$

where ϕ_0 is the unquenched quantum yield, ϕ_q is the quantum yield with quencher present, (Q) is the concentration of quencher, k_d is the unimolecular rate of triplet decay, k_q is the bimolecular rate of quenching, and k_r is the desired unimolecular rate of triplet rearrangement.[15] Solution of eq 3 indicates that with $k_r = 4 \times 10^8$ sec^{-1} quenching would be observed. It is therefore likely that the rate of dienone triplet rearrangement to bicyclic ketone is 10^{10} sec^{-1} or greater. Thus this is not only an exceedingly efficient photochemical rearrangement but also one in which the excited state involved rearranges at a particularly rapid rate.[16]

Thus, as pointed out in our preliminary communication,[4] the absence of quenching by naphthalene cannot be construed in a unimolecular reaction to mean that a triplet is not involved. Rearrangement may just be too rapid for diffusion of the excited state to quencher molecules.

Although naphthalene at maximum usable concentrations gave no quenching within experimental error, the use of piperylene as solvent resulted in nearly or totally complete quenching. A similar observation has been made by Fisch and Richards[7] in the case of the santonin to lumisantonin reaction. Quenching of a reaction by piperylene solvent has been commonly taken as evidence that the reaction must proceed *via* a triplet. The argument rests on the assumption that the high energy of piperylene excited singlet[18] makes it unlikely that a singlet ground-state piperylene molecule could accept energy from a typical excited singlet carbonyl compound.

Nevertheless, piperylene was found to be less than a perfectly satisfactory test for triplets. Dienone reactant was consumed to some extent in a process not leading to bicyclic ketone. The reaction mixture became

---

typical diffusion rates), the pseudo-unimolecular rate of singlet excitation transfer becomes *ca.* 10^7 sec^{-1}. However, this is slow compared with the rate of acetophenone singlet decay by intersystem crossing which is at least 10^{10} sec^{-1}.[10] Allowing an order of magnitude margin of error, at most 1% of the acetophenone singlets would be capable of energy transfer. In this argument the assumption of collisional rather than long-range transfer of acetophenone singlet excitation seems reasonable in view of the not fully allowed nature of the $n-\pi^*$ acceptor and donor transitions (note ref 9 for discussion of this point). Also ref 10 provides evidence against singlet excitation transfer from acetophenone excited singlet to biacetyl at concentrations of the same order as presently employed.

(9) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(10) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 3080 (1963).

(11) Since the intersystem crossing efficiency of acetophenone excited singlet is essentially unity (note ref 1, footnote 13, for summary of references and evidence), the sensitized quantum yields represent the efficiency with which the triplet of dienone **1** rearranges to bicyclic ketone **2**.

(12) The quantum yield in presence of 0.1 *M* naphthalene is slightly low. While this difference may be real, it is within experimental error which in this case is likely to be more troublesome owing to the large amount of naphthalene to be separated.

(13) The triplet energy of dienone is 68.8 kcal/mole while that for acetophenone is 73 kcal/mole. Triplet transfers exothermic by more than 3 kcal/mole seem to be diffusion controlled,[14] and the assumption seems presently justified.

(14) (a) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962); (b) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).

(15) Note ref 1 for a similar argument and more details.

(16) Compare the type-A rearrangement of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone whose triplet transformation has a $k_r = 2.9 \times 10^5$ sec^{-1}.[17]

(17) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966).

(18) The energy of piperylene's lowest excited singlet has often been taken from its ultraviolet maximum at 2300 A.[7,19] Recently, the suggestion has been made[20] in the related case of butadiene that the maximum does not afford a valid approximation to the energy and the 0–0 level of the singlet may be as low as 90 kcal/mole. Piperylene excited singlet should be similar.

(19) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(20) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965).

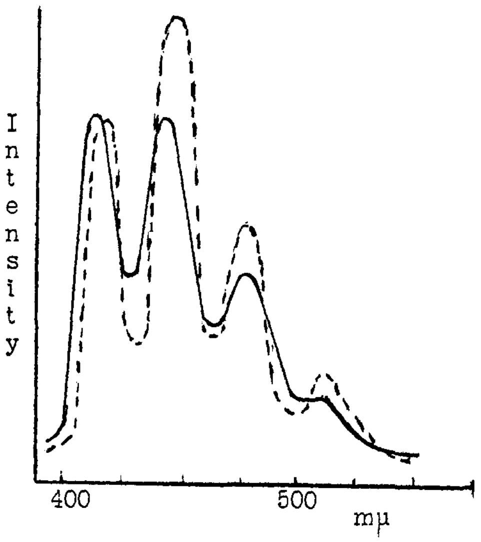


Figure 1. Triplet emission spectra: ———, dienone; - - - -, benzophenone.

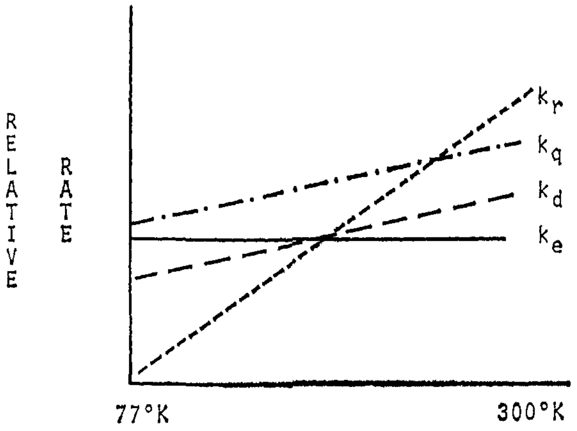


Figure 2. Temperature dependence of dienone processes.

progressively more opaque in the ultraviolet,[21] although not enough so to account for total inhibition of bicyclic ketone formation. Finally, there is the point that when a quencher constitutes the solvent cage surrounding an excited state, it is possible that singlet excitation might be transferred to the cage, perhaps to form a singlet excimer. We conclude that quenching by piperylene provides some additional evidence in favor of a triplet dienone to bicyclic ketone route. The rigor of the piperylene test awaits further evidence on such quenching.[22]

Evidence for the Presence of the n–π^* Triplet. The phosphorescence emission spectrum of 4,4-diphenylcyclohexadienone in EPA at 77°K is given in Figure 1 along with that of benzophenone which is provided for comparison. The spacing between the 0–0, 0–1, 0–2, and 0-3 bands averaged 1638 cm^{-1}, corresponding either to the 1658-cm^{-1} ground-state carbonyl stretching frequency or the 1618-cm^{-1} ground-state C=C stretching. This well-defined vibrational pattern has been noted by Ermolaev and Terenin[23a] and by Kasha[23b] to be characteristic of phosphorescence emission from n–π^* triplets.[24] This criterion should be construed as providing strong sufficient but not necessary evidence for the emission coming from an n–π^* species. Thus it appears that relatively symmetrical ketones and those with few conformationally mobile bonds tend to have well-defined n–π^* vibrational structure; however, the less symmetrical and more flexible n–π^* species may give poorly defined emission resembling that of π–π^* triplets.[25]

The lifetime of the triplet of 4,4-diphenylcyclohexadienone was determined at 77°K in EPA glass as 0.5 msec. In ethanol–ether the lifetime was 0.4 msec. This relatively short triplet lifetime is in the range expected for n–π^* triplets but short for a π–π^* triplet. Thus McClure has reported[26] lifetimes of 0.85 msec for methyl ethyl ketone, 0.95 msec for diethyl ketone, and 5 msec for benzophenone; in contrast, he found a value of 950 msec for 2-acetonaphthone and Pitts found[27] a value of 270 msec for Michler's ketone. It is well accepted that of these only the last have π–π^* configurations for the lowest energy triplet.

The preceding evidence based on vibrational structure and lifetime of the phosphorescence emission indicates the presence of the n–π^* triplet at low temperature. This suggests but does not prove that it is the n–π^* triplet which is present and reacts at room temperature.

One experiment of interest was the photolysis of 4,4-diphenylcyclohexadienone in an ether–pentane–ethanol glass at 77°K. A control run was made in the same solvent at room temperature. Although 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**) was formed in the control run, no reaction of any kind was detectable at 77°K. Also, it had earlier[28] been observed that in EPA glass at 77°K the phosphorescence emission of 4,4-diphenylcyclohexadienone is quenched by naphthalene; this is in contrast to the lack of quenching by naphthalene of the rearrangement at room temperature. The inhibition of rearrangement at low temperature can be construed as evidence for some, however small, activation energy in the triplet rearrangement. The above facts are summarized in Figure 2, which depicts the rates of rearrangement (k_r), of naphthalene quenching (k_q),

---

[21] In studies where piperylene quenching has been interpreted as evidence for a triplet excited state, there generally seems to be no evidence reported about optical density changes. Not only in this special case, but, in general, the solutions should be monitored to detect development of products and impurities acting as internal filters and thus giving false quantum yields and spurious quenching.

[22] Note the recent report of L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966), of quenching of naphthalene singlet by piperylene. In view of the recent singlet energy suggested[18] for piperylene, this transfer seems not to be highly endothermic as originally thought. The dienone singlet to piperylene transfer is, however, much more endothermic.

[23] (a) V. Ermolaev and A. Terenin, *Opt. i Spektroskopiya*, **1**, 523 (1956); (b) M. Kasha, *Radiation Res. Suppl.*, 2, 265 (1960).

[24] MO calculations suggest that the bond order changing most on n–π^* excitation is C–O. Hence the excited singlet potential energy minimum will be displaced along a C–O bond length coordinate from the ground-state minimum. The result is that nearly vertical demotion with emission will be to a number of ground-state vibrational levels differing in 1 quantum of C–O stretching vibration. In π–π^* excited states more bonds differ in length from the ground state and more vibrational states may result on electron demotion.

[25] The phosphorescence emission of santonin[7] has been reported to consist of a broad band. It seems unlikely that this dienone and 4,4-diphenylcyclohexadienone differ in the configuration of the lowest triplet. A more likely source of difference is the availability of complex vibrations in the unsymmetrical santonin molecule.

[26] D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949).

[27] J. N. Pitts, H. W. Norman, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

[28] Unpublished results of H. E. Z. and R. Keese.

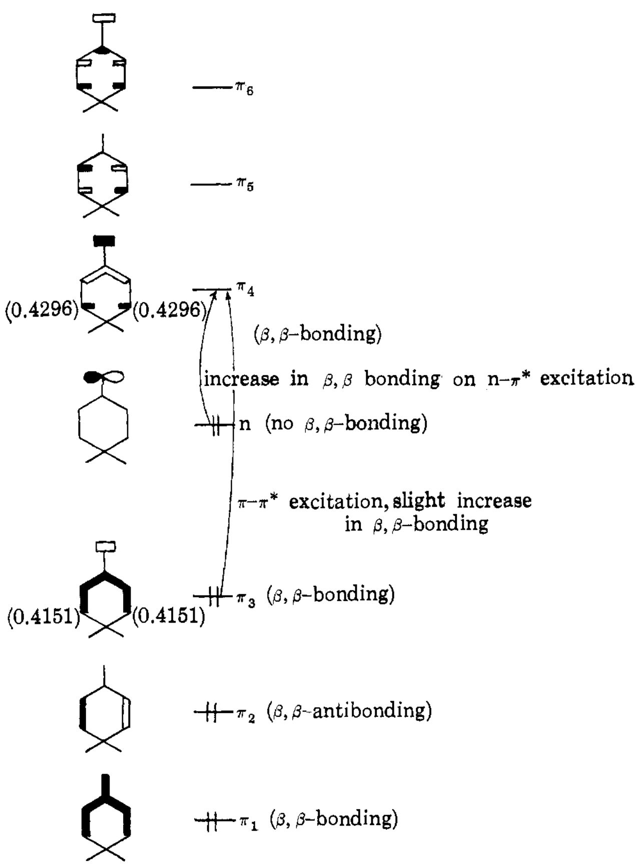


Figure 3. Cyclohexadienone molecular orbitals and electronic excitation processes: ■, wave function positive; □, wave function negative.

of unimolecular triplet decay (k_d), and of phosphorescence emission (k_e), all as a function of temperature.[29]

One further piece of evidence pointing to reaction of an n–π^* triplet is theoretical in nature. The type of bonding occurring in the reaction is anticipated on MO grounds for an n–π^* excited state but not for a π–π^* species. Specifically, formation of a bond between carbons 3 and 5 (*i.e.*, β,β bonding) has been proposed by us as the first step following formation of the n–π^* excited state;[3,4,30,31] concrete support for this proposal is the presence of this new bond in the product.

The six π molecular orbitals and the one p_y (*i.e.*, n, nonbonding) orbital are depicted schematically in Figure 3. The MO's were obtained from a Mulliken–Wheland–Mann SCF-type calculation.[32] It is seen that there is an increase in β,β-bond order (*i.e.*, between atoms 3 and 5) on n–π^* excitation, since the electron promoted goes from the nonbonding p_y orbital to the first antibonding molecular orbital, π_4, which has a positive sign for the wave function above the molecular plane at both β carbons. In contrast, π–π^* excitation removes an electron from π_3 which is already β,β-bonding (*i.e.*, like signs at the β carbons) and promotes the electron to π_4. Scrutiny of the LCAO MO coefficients given in Figure 3 reveals only a slight increase in β,β-bond order on π–π^* excitation. Thus the β,β-bond order per electron in π_3 is $C_{33}C_{53} = +0.1725$, while that in π_4 is $C_{34}C_{54} = +0.1846$. The total β,β-bond orders calculated for ground, n–π^* excited, and π–π^* excited states are depicted in Figure 4. We note that of these bond orders only the n–π^* one is bonding; the β,β-interaction is antibonding in both the ground and π–π^* excited states. Accordingly, the observed β,β-bonding is consonant with the expected behavior of only the n–π^* excited species.[33,34]

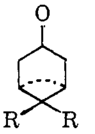


Figure 4. β,β-Bond orders for various dienone states: Total β,β-bond order, - - - -; for ground state, −0.07038; for π–π^* excited state, −0.05828; for π–π^* excited state, +0.1142.

Electronic Details of the Transformation. *A priori* one might envisage pathways included in Chart I as available in leading 4,4-diphenylcyclohexadienone (**1**) to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**). The "circle, dot, y" notation is that used earlier to represent sp hybrid electrons, π-system electrons, and nonbonding p_y electrons, respectively.[1,3,30] In the chart, the ground-state species are given at the bottom with each excited-state species above its ground-state counterpart.[39] The specific problem at hand is one of

---

(29) There are no quantitative implications and thus no reason to assume a temperature where all rates are equal.

(30) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, Abstracts, p 31.

(31) H. E. Zimmerman, *Advan. Photochem.*, **1**, 3 (1963).

(32) These results are qualitatively in accord with configuration interaction calculations by H. E. Zimmerman and R. W. Binkley, unpublished; here the triplet-state bond orders are used for comparison.

(33) The approximation using bond orders between atoms assumed not to overlap appreciably in the original LCAO MO calculation is valid as one criterion of tendency to bond. This is equivalent to a first-order perturbation treatment where the energy change on allowing such bonding is given by $E = \Sigma n_k C_{rk} C_{sk} \beta_{rs} = P_{rs}\beta_{rs}$. We note β is negative, n_k is the number of electrons in MO k, and r and s refer to the atoms whose bonding is under consideration. A predominance of like sign ($C_rC_s > 0$) overlap signifies stabilization. This test of bonding *vs.* antibonding tendencies of two atoms was first applied to photochemistry[30] to account for the formation of cyclobutenes from dienes, but there[30] only the *change* in bond order was taken into account.[34]

(34) Similar reasoning, but utilizing the bonding *vs.* antibonding tendency of only the highest occupied MO, has been applied to the photochemistry of hexatrienes by Oosterhoff,[35] by Zimmerman[36] for the Sommelet and Stevens ground-state processes, and by Woodward and Hoffman[37] for predicting the stereochemistry of electrocyclic closures.[38]

(35) L. G. Oosterhoff, quoted in E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 151 (1961).

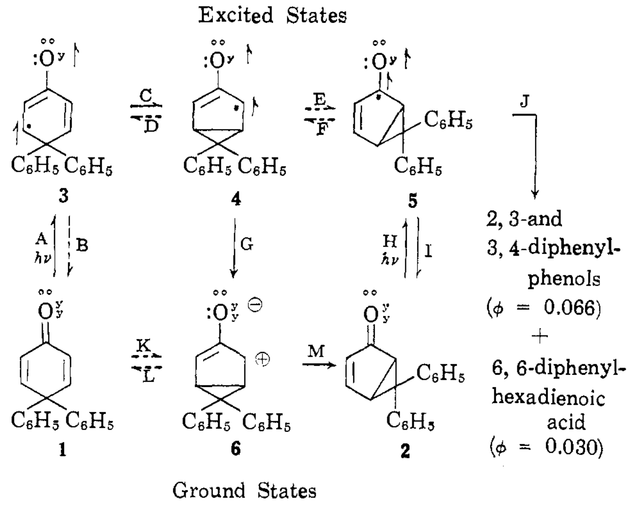
(36) H. E. Zimmerman in "Molecular Rearrangements," Vol. I, Interscience Publishers, New York, N. Y., 1963, p 388, and *errata*.

(37) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965).

(38) The use of change in bond order on excitation tells only whether bonding is more or less favorable in the excited state than in the ground state, and the present additional use of total bond order is helpful. The use of only the highest occupied MO's symmetry does not invariably agree with the total energy change on bonding as is evident in the present dienone example; here the highest occupied MO is common to *both* the π–π^* and n–π^* excited states. Yet the over-all bond order is negative (antibonding) in the π–π^* excited state and positive (bonding) in the n–π^* configuration. The highest occupied MO in the ground state is bonding, but the over-all β,β-bond order is negative. For the special systems studied by Woodward and Hoffman,[37] the highest occupied MO does provide a correct prediction for definite but less than obvious reasons. Thus, for example, in the case of the excited state of hexatriene, the antibonding contribution to disrotatory 1,6-overlap in the highest (singly) occupied MO ψ_4 is exactly counterbalanced by the bonding effect of the next lower (singly occupied) MO ψ_3. Hence it is the competition between the antibonding contribution of ψ_2 and the bonding effect of ψ_1, and the former dominates.

(39) The notation used in Chart I may seem cumbersome. Nevertheless, its utility is presently demonstrated and such or equivalent notation is required when it is operationally possible to distinguish between different electronic configurations of reacting species. For example, the relationship between excited state **4** and ground-state **6** is specified. Especially in the case of the singlet counterpart of **4** the use of the common "dot–dot" notation would allow interpretation as merely a resonance contributor to **6**. For π–π^* excited states of species without nonbonding electrons, the present representation becomes identical with "dot–dot" structures.

Chart I



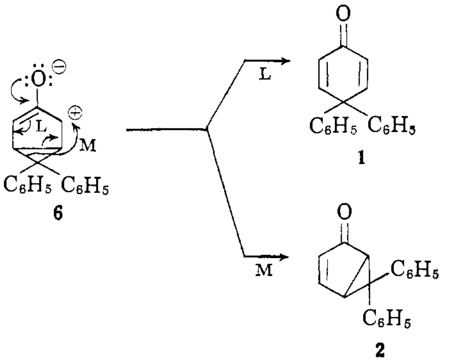
determining which route is followed in the conversion of 4,4-diphenylcyclohexadienone (**1**) to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**2**). However, the problem is more general.

Thus, it is of more than limited interest to know how excited-state reactants get to the ground-state products observed in photochemical reactions. One would like to know at which stage the electronic excitation is lost and how. In the present instance one might inquire whether the excited state (**5**) of the final bicyclic ketone product (**2**) is formed with all rearrangements (steps C and E) occurring in the excited state, followed by electron demotion (process I) to bicyclic ketone. Alternatively, loss of excitation might occur with demotion taking place before the geometry of the final product is obtained, If demotion takes place after initial excited-state bridging (*i.e.*, bridging by process C followed by demotion G), then mesoionic zwitterion **6** is generated. In the past we have postulated that such mesoionic zwitterions are responsible for much of dienone photochemistry.[3,30,39]

Indeed there is evidence showing that the excited state (**5**) of bicyclic ketone product cannot be reached and that demotion must take place at an earlier stage. Thus, the quantum efficiencies with which triplet excited-state **5** proceeds onward (step J) to 2,3-diphenylphenol, 3,4-diphenylphenol, and 6,6-diphenylhexadienoic acid are known.[1] If this excited state is formed it must react further with this characteristic efficiency (ϕ = 0.030, 6,6-diphenylhexadienoic acid from triplet, ϕ = 0.066, diphenylphenols from triplet). However, in very low conversion runs designed to minimize product absorption, only small quantities of the 6,6-diphenyl-3,5-hexadienoic acid and diphenylphenol products were formed (ϕ = 0.010 for the acid and ϕ = 0.032 for the phenols). This means that the excited state of bicyclic ketone product cannot be the general precursor of **2** although it is not possible to exclude some of the reaction following this route. While, of course, demotion can in principle occur anywhere prior to the point where excited-state **5** is formed, it is useful to consider as an approximation that demotion takes place following step C when species **4** is formed; **4** is the n–π^* excited state of the mesoionic zwitterion **6**.

Further information is available concerning the pathways utilized by the reacting species. Thus the high quantum yield, ϕ = 0.85, requires that most molecules efficiently proceed in the forward direction. This means that pathways B, D, and L are relatively unimportant. Since it seems unlikely that the reaction is one of the electronically unexcited but vibrationally excited reactant,[40] pathway K is assumed not to be utilized. Another relevant point derives from our present and previous[1] observation that irradiation of bicyclic ketone **2** affords no dienone **1**, showing that process F or L or both are unfavorable. We are left with the route A–C–G–M which is the mechanism proposed in our original studies on dienone rearrangements.[3,30]

There is one interesting question which arises and this is why zwitterion **6** undergoes process M leading to bicyclic ketone **2** in marked preference to reversion to dienone **1** (*i.e.*, process L). An upper limit of 15% is imposed on process M by the 0.85 quantum yield, and it is likely that the less than unity quantum yield has other sources of inefficiency such as radiationless transitions to reactant. Yet the organic chemist practiced at "electron pushing" finds arrow notation leading from zwitterion **6** to dienone **1**. Process L is the ground-state reverse of the excited-state process affording zwitterion **6**. While overlap is not perfect, the p orbitals at carbons 2 and 6 (cyclohexane numbering) can overlap with the banana-bond orbitals comprising three ring σ bond 3–5 as is necessary for process L.



process M preferred over L

Consideration of the molecular orbital correlation diagram for the dienone–zwitterion interconversion process is helpful in rationalizing this enigma and also in understanding the photochemical transformation itself.

The MO's are depicted qualitatively in Figure 5.[42,45] We

---

[40] In the case of 4,4-diphenylcyclohexadienone, it has been shown[28] that pyrolysis in 75% aqueous dioxane gives exclusively 3,4-diphenylphenol and not the product distribution observed photochemically. The argument has been used by Zimmerman and Schuster[3b] that products obtained by pyrolysis should be observed photochemically if the mechanism involves demotion to a vibrationally excited (*i.e.*, "hot") ground state which undergoes a thermal transformation. The argument assumes a very rapid repartition of vibrational energy of the photochemically formed and demoted species, since the initial vibrational excitation may be localized in a particular bond or in a manner not attained thermally, and repartition of vibrational energy seems likely to be exceedingly facile. Additionally, it has been pointed out on a theoretical basis that in solution photochemistry, except where exceedingly low-energy ground-state processes are available or where the molecule has very few bonds to accept vibrational energy, collisional deactivation by solvent is likely to be much faster than a hot ground-state molecule reaction.[41]

[41] H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

[42] The calculations were carried out initially on the π system assuming separation from the σ framework, which of course is strictly not correct. The qualitative validity was checked by three-dimensional calculations[43] using the general method of Lipscomb and Hoffmann.[44]

note that the ground state of zwitterion **6** (on the right) leads to a doubly excited state of dienone if an adiabatic transformation (right to left) is considered. Although it is likely that there will be a change in occupation as the point is reached where MO's ψ_4 and ψ_5 cross, nevertheless the fact that the system must approach such a high energy state must introduce a considerable activation energy and make the reversion of zwitterion to dienone difficult.[46]

Still another point deals with the mode of electron demotion. It has been suggested by Zimmerman[49] that electron demotion in photochemical reactions may, in cases, take place at the point where the excited-state and ground-state potential energy surfaces cross and that in the Hückel approximation this is where the two odd-electron-containing MO's intercept. Accordingly, we note on referring to Figure 5 that demotion may occur somewhat prior to species **4** actually being reached. In any case the antibonding electron in MO ψ_5 and the electron in partially vacant ψ_4 are in orbitals which overlap and which are considerably compressed in space with the result of an enhanced demotion probability.[50]

Singlet Sensitization. In our earlier studies on the photochemistry of 4,4-diphenylcyclohexadienone,[4] it was observed that the relative conversions of dienone to product on photolysis in benzene were increased when naphthalene was added. In these runs lacking nucleophiles to consume the ketene of 6,6-diphenylhexadienoic acid, the solutions were observed to become opaque in the 310–360-mμ region irradiated. Since naphthalene absorbed appreciable light in this region, it seemed certain that energy was being transferred from absorbing naphthalene to dienone reactant. Several explanations were considered, and it is now shown that the energy transfer was by singlet sensitization.

For this work a filter transmitting in the 280–340-mμ region was employed along with naphthalene concentrations of 0.213 *M* in aqueous dioxane; this allowed 85% of the incident light to be captured by naphthalene. With a dienone concentration of 0.00335 *M*, a quantum yield of 0.28 was obtained; a higher ϕ of 0.37 resulted with 0.00597 *M* dienone. That naphthalene was not transferring energy from its triplet was shown in a run employing 0.063 *M* piperylene[51] together with 0.213 *M* naphthalene; a quantum yield of 0.26 resulted, showing no piperylene quenching.

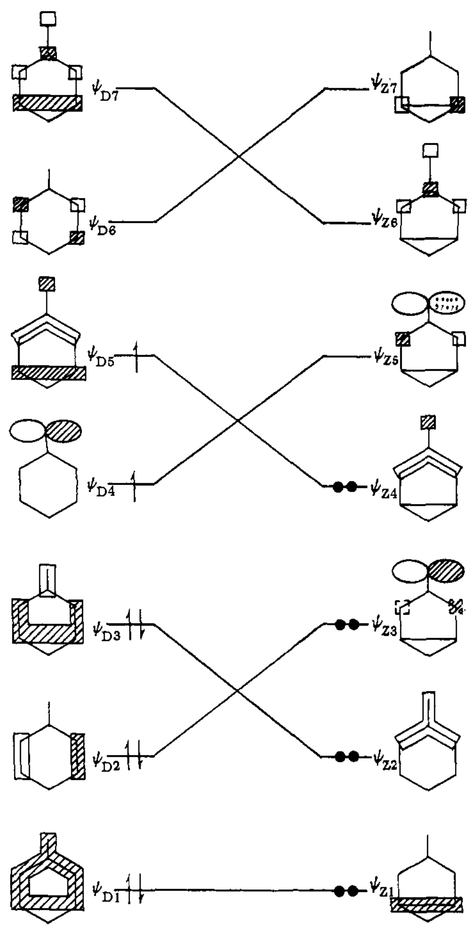


Figure 5. MO correlation diagram for closure of dienone to 3,5-bridged species; wave function positive, ■; wave function negative, □. Electrons in levels occupied in dienone n–π* triplet ↿ or ⇂; electrons in levels occupied in ground-state zwitterion, ●.

In view of the 0.85 quantum yield for the ordinary dienone reaction and considering the 15% of the light absorbed directly by dienone in these naphthalene experiments, the efficiency of naphthalene transfer of singlet excitation under the conditions employed is 35–40% at best.

The ability of naphthalene to transfer singlet excitation was substantiated by dienone quenching of naphthalene fluorescence.[53] It was found that 0.00280 *M* dienone quenched the fluorescence to *ca.* one-quarter.

MO's ψ_{Z3} and ψ_{Z5} are modified[45] in Figure 5 to accord with the three-dimensional calculations.

(43) H. E. Zimmerman and R. W. Binkley, unpublished; R. W. Binkley, Ph.D. Thesis, University of Wisconsin, 1966.

(44) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963); **40**, 2474, 2480, 3247 (1964).

(45) The simple π calculation leads to correlation of ψ_{D2} with $-\psi_{Z5}$ and ψ_{D4} with ψ_{Z3}. In the three-dimensional calculation ψ_{D2} and ψ_{D4} differ in symmetry and do not interact. As soon as β,β bonding begins, symmetry with respect to the plane of the paper disappears and these MO's become admixtures. That is, MO's ψ_{Z3} and ψ_{Z5} now have the same symmetry, and both have π and p_y components. This arises since there is interaction around the out-of-plane three ring among the orbitals making up this ring. Some of these three-ring orbitals overlap with the π system and some with the σ system which in turn overlaps with p_y. Thus a Hückel ψ_{Z3} and ψ_{Z5} can interact. This means that as soon as the β carbons of the dienone species begin to approach one another with carbon-4 bending out of plane, the p_y and π orbitals begin to admix.

(46) Note ref 47–49 for use of MO and state correlation diagrams.

(47) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(48) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4389 (1965).

(49) H. E. Zimmerman, *ibid.*, **88**, 1564, 1566 (1966).

(50) In no sense does electron demotion involve any difficulty as has sometimes been inferred from the presence of the antibonding electron at carbon-2 in structure **4** contrasted with the demoted electron being at the oxygen in **6**. It should be recognized that **4** is merely one of several resonance structures and that the antibonding electron (as well as the nonbonding p_y one) is actually distributed.

(51) The ability of piperylene to quench naphthalene triplet has received experimental support from the work of Hammond.[52] Thus despite the similar triplet energies of piperylene and naphthalene some transfer should occur with a diminution in quantum yield if the naphthalene to dienone transfer were of the triplet variety. Indeed, owing to piperylene's lower triplet energy (61 kcal/mole) and higher concentration relative to dienone, we can conclude that triplet transfer to piperylene would occur in preference to transfer to dienone. The concentration of piperylene used was insufficient to allow serious naphthalene singlet destruction (*cf.* ref 22).

(52) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965)

(53) The work of J. B. Aladekomo and J. B. Birks, *Proc. Roy. Soc.* (London), **284**, 551 (1965), shows that at the high naphthalene concentration used a reasonable portion of the fluorescence may be from the singlet excimer. Similarly, sensitization could be by the excimer. This does not change the interpretation and utility of singlet sensitization.

The complete data are given in the Experimental Section.

It should be noted that singlet sensitization by high extinction coefficient absorbers has a practical consequence. In many reactions of synthetic interest the accumulation of strongly absorbing impurities or products prevent reasonable conversion to product.[54] Use of a singlet sensitizer whose extinction coefficient allows it to compete effectively for the light then obviates the difficulty and allows reaction. Additionally, when the singlet sensitizer is a triplet quencher as well, one should be able selectively to inhibit triplet processes simultaneously, thus allowing study of singlet photochemistry.

Experimental Section[55]

6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one, 3,4-Diphenylphenol, 2,3-Diphenylphenol, and 6,6-Diphenyl-3,5-hexadienoic Acid. These compounds were prepared and purified as previously described.[1,3]

Apparatus and Quantum Yield Procedures. For both preparative and quantum yield photolyses the macro photolysis cells, 5.0 cm deep and 12 cm in diameter described earlier,[1] were used in conjunction with the triple compartment filter cell.[1] All runs were made at 25.0 ± 0.1°. Light output was monitored with a phototube to check for lamp decay and filter decomposition. The filter solutions and general actinometric procedure described in our earlier publication[1] were employed. Products were isolated by liquid–liquid partition chromatography as before.

In sensitized runs acetophenone was removed prior to chromatography by distillation at 30–34° and 0.05 mm. In runs with naphthalene this compound was removed by sublimation at the same temperature and 0.1 mm. In some cases, naphthalene was first recrystallized from the mixture. It was ascertained that no photochemical products were removed with the acetophenone or with the naphthalene. The crude reaction mixture was dissolved in ether–chloroform and washed with water, the photoacid was extracted with 5% sodium hydroxide, and the organic layers were washed with water, dried over sodium sulfate, and concentrated *in vacuo*. The basic extracts were acidified to congo red with dilute sulfuric acid and ether extracted. The extracts were washed with water, dried, and concentrated under vacuum to give the photoacid which crystallized. The neutral fraction was subjected to liquid–liquid partition chromatography;[1,3] fractions were weighed and then identified by melting point, infrared, and nmr. Nmr proved useful in establishing purity.

Immediately after each run the ultraviolet spectrum was taken between 310 and 400 mμ to establish the absence of light-absorbing impurities. Optical densities calculated from dienone and bicyclic ketone isolated were within 2–6% of theory down to 330 mμ. The ultraviolet spectrum below 330 mμ had an additional contribution from the photoacid and the diphenylphenols. In sensitized runs an added check was derived from the ratio of the vinyl nmr peaks of dienone and bicyclic ketone; the agreement with isolation was within 4%. Mass balances were 97% or better in acceptable runs with the exception of the piperylene work where 93% was recovered. Quantum yields were based both on bicyclic ketone produced as well as on dienone consumed. Filter A[1] (320 mμ, 0% transmission; 330, 5%; 350, 53%; 380, 7%; 390, 1%) was used in unsensitized runs. In acetophenone-sensitized runs, filter B[1] (305 mμ, 0% transmission; 310, 4%; 330, 50%; 360, 5%; 370, 0%) was employed. For naphthalene sensitizations filter F[1] (280 mμ, 0% transmission; 290, 11%; 310, 38%; 330, 5%; 340, 0.5%) was utilized. Where it was of interest to determine the amount of light captured by different substances, the relative light absorbed by each component was integrated over 10-mμ intervals taking into account at each wavelength the relative concentration, the relative extinction coefficient, the filter transmission, and lamp output.

Low-Temperature Photolysis. A 3-ml portion of 0.0809 g of 4,4-diphenylcyclohexadienone in 6.0 ml of 2:1 ethanol–ether was degassed in a 1.0 × 20 cm Pyrex tube in a quartz dewar containing liquid nitrogen. Irradiation was carried out for 43 min using a 450-w high-pressure lamp and an air stream preventing fogging of the apparatus. The solid product was subjected to crystallization; both the first crop and the mother liquors afforded only starting dienone and the infrared gave no trace of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one absorption.

In a control run differing in the absence of liquid nitrogen the infrared showed absorption due to both dienone reactant and bicyclic ketone product; nmr analysis gave a ratio of 2.5.

Quenching of Naphthalene Fluorescence. Measurements were made in an Aminco-Kiers spectrofluorometer modified to minimize scattered light. Measurements were in a square quartz cell with excitation at 310 mμ. The fluorescence decrease was not due to absorption of light by added ketone which was less than 1% at 3.14 m*M* dienone. Stern–Volmer plots at low dienone concentration (0.220–3.33 m*M*) were linear while higher concentrations gave curved plots. Ketone was dissolved in 0.218 *M* naphthalene in 69% aqueous dioxane to give the following results: at 345 mμ, F_0/F = 1.00, 0.00 m*M* dienone; 1.18, 0.220 dienone; 1.38, 0.450; 1.82, 1.105; 2.40, 1.750; 3.04, 2.320; 3.56, 2.840; 4.72, 4.720. Run 2: F_0/F = 1.13, 0.203 m*M* dienone; 1.21, 0.406; 1.35, 0.569; 1.53, 0.796; 1.96, 1.380; 3.03, 2.440; .405, 3.330. Additional runs gave similar results. Naphthalene fluorescence quenching was also observed for 4,4-diphenylcyclohex-2-en-1-one and for 4,5-diphenylcyclohex-2-en-1-one.

Acknowledgment. Support of this research by a National Science Foundation predoctoral fellowship for J. S. S., NSF Grant GP-1966, and the Wisconsin Alumni Research Foundation are gratefully acknowledged.

---

[54] Many of the reactions described in the literature as requiring excessive irradiation times seem likely to derive from this effect. The photochemist does well to monitor ultraviolet absorption to determine when no further light is being absorbed by reactant and when conversion to product has ceased.

[55] All melting points were taken on a hot-stage apparatus and are corrected.