

imidazole ligand of methylcobalamin,<sup>32</sup> which has a significant influence on the rate of displacement of cobalt by mercury(II); (iv) protonation of a cyanide ligand of alkylpentacyanocobaltates **59** which induces a unimolecular rearrangement to an insertion product **60**,<sup>89,90</sup> and (v) protonation of cyanide ligands of organo(cyano)cobaloximes **61** which leads to bridged complexes **62** and **63**.<sup>91,92</sup>

(89) M. D. Johnson, M. L. Tobe, and L. Y. Wong, *J. Chem. Soc. A*, 923 (1968); 929 (1968).

(90) J. Kwiatek, *Catal. Rev.*, 1, 37 (1967).

These reactions, and those of the former class, serve one particularly useful purpose: they illustrate that the reactivity of carbon-metal bonds toward electrophiles is not inherently greater than that of other organic molecules but depends much upon the exact nature of the molecules concerned.

*I acknowledge with gratitude my debt to the co-workers named in the references and to many friends for stimulating discussions!*

(91) A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 14, 486 (1975).

(92) D. Dodd and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 1218 (1973).

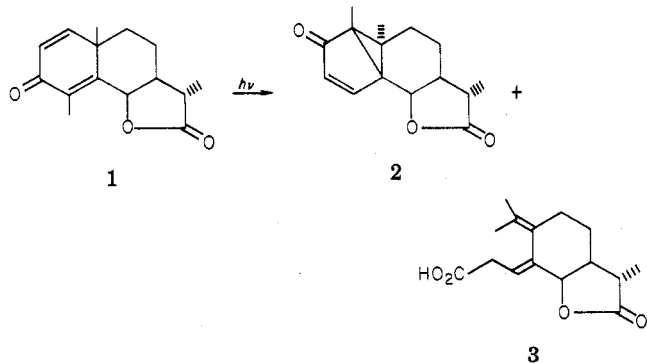
## Mechanisms of Photochemical Transformations of Cross-Conjugated Cyclohexadienones

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Received January 10, 1977

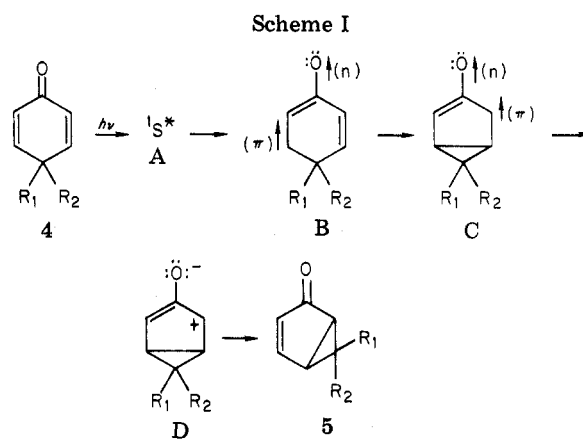
Cross-conjugated cyclohexadienones have been subjected to intensive photochemical studies for many years. Originally, these compounds fascinated organic chemists because of the deep-seated rearrangements which occurred when irradiated with ultraviolet light in the 250–370 nm region, typified by the conversion of santonin (**1**) to lumisantonin (**2**) and to photosantonin



acid (**3**).<sup>1</sup> The extensive studies which elucidated the sequence of thermal and photochemical events involved in these and other complex transformations have been summarized in several reviews.<sup>2</sup>

Following the pioneering studies by Barton, Jeger, van Tamelen, and their groups which established the structures of the photoproducts of santonin and related steroid dienones, a unifying mechanistic concept was proposed in 1961 and 1962 by Zimmerman and this author<sup>3</sup> which satisfactorily rationalized the nature of the primary processes occurring on irradiation of such

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dienones (Scheme I). Thus, the formation of bicyclo[3.1.0]hexenone (**5**) from a model 2,5-cyclohexadienone (**4**) was postulated to occur in a series of events involving (a) formation of the  $n,\pi^*$  singlet excited state, symbolized as A, (b) intersystem crossing to the triplet  $n,\pi^*$  state B, (c) bridging ("rebonding") to give C, which is still an electronically excited molecule of the  $n,\pi^*$  type, (d) electron demotion to give the ground-state zwitterion D, and finally (e) rearrangement of D to lumiketone **5**, a process subsequently designated a sigmatropic shift of order [1,4]. Precedent and theory were cited for all of these steps. Furthermore, this approach was successful in rationalizing the formation of rearranged products (phenols and ketones) involving

(1) (a) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, 40, 1732 (1957); (b) D. H. R. Barton, P. de Mayo and M. Shafiq, *Proc. Chem. Soc.*, 205, 345 (1957); *J. Chem. Soc.*, 929 (1957); 140, 3314 (1958); (c) E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky and P. Aldrich, *J. Am. Chem. Soc.*, 80, 501 (1958); 81, 1666 (1959).

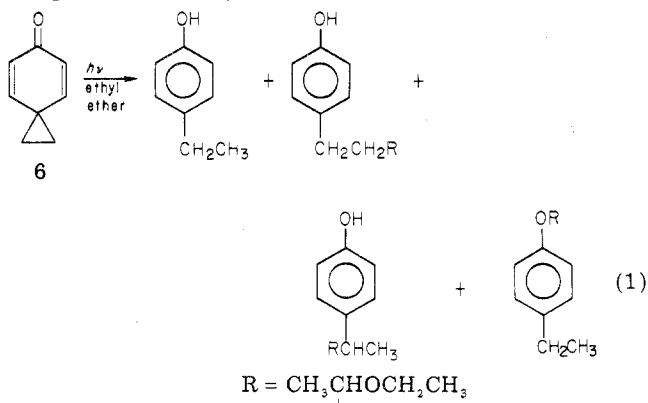
(2) For reviews, see (a) H. E. Zimmerman, *Adv. Photochem.*, 1, 183 (1963); (b) O. L. Chapman, *ibid.*, 1, 323 (1963); (c) K. Schaffner, *ibid.*, 4, 81 (1966); (d) P. J. Kropp, *Org. Photochem.*, 1, 1 (1967); (e) O. L. Chapman and D. S. Weiss, *ibid.*, 3, 197 (1973).

(3) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, 83, 4486 (1961); 84, 4527 (1962).

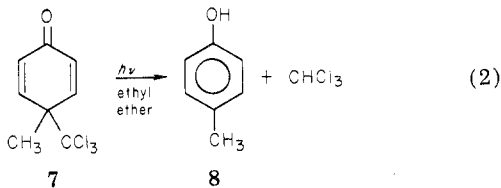
secondary transformations of lumiketones **5**.<sup>2a,3</sup>

We set out some years ago to establish experimentally various features of this proposed mechanism, using the full arsenal of techniques available to the contemporary photochemist. We have been successful in achieving this goal to a large extent, although solutions to certain aspects of the problem remain elusive.<sup>4,5</sup>

Our initial goal was to obtain experimental support for the description of the dienone excited state A as essentially a diradical species,<sup>3</sup> since it had been suggested<sup>2b</sup> that the photochemistry of these systems could be adequately described in terms of transformations exclusively of "polar state" intermediates. Some model cyclohexadienones were sought where free-radical reactions of the excited state(s) might compete with decay to the proposed zwitterion D. We first studied the spirodienone **6** and demonstrated that its photochemistry involved reactions (eq 1) charac-



teristic of free-radical intermediates, and was therefore incompatible with a polar description of the excited state.<sup>6</sup> However, one could object that because of ring strain the behavior of **6** represented a special case. A better model compound, also possessing a C<sub>4</sub> substituent which could be expelled as a radical, was required. Dienone **7**, which has not only an appropriate substituent (CCl<sub>3</sub>) but also the virtues of molecular simplicity and ease of synthesis, was chosen for intensive study. In short order, Patel established that irradiation of **7** in ethyl ether and other solvents gave the desired reaction (eq 2), namely formation of *p*-cresol (**8**) and



products derived from CCl<sub>3</sub>· (CHCl<sub>3</sub> or C<sub>2</sub>Cl<sub>6</sub>), supporting a description of the primary photochemical intermediate as a radical-like species.<sup>7</sup>

Patel soon discovered that other photoproducts were formed from dienone **7** in various solvents, including lumiketone **9**<sup>8</sup> (analogous to lumisantonin (**2**)) and ethers **10** and **11** apparently arising from ionic reactions

(4) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **90**, 5145 (1968).

(5) D. I. Schuster, G. C. Barile, and K.-C. Liu, *J. Am. Chem. Soc.*, **97**, 4441 (1975).

(6) (a) D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **86**, 4502 (1964); **88**, 1722 (1966); (b) D. I. Schuster and I. S. Krull, *ibid.*, **88**, 3456 (1966).

(7) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **87**, 2515 (1965).

(8) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **88**, 1825 (1966).

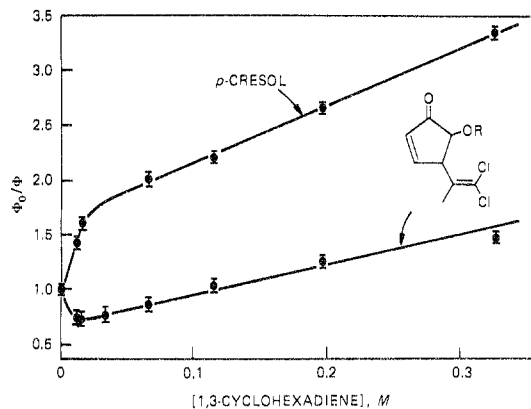


Figure 1. Effect of added 1,3-cyclohexadiene on product yields from photolysis of dienone **1** in 2-propanol.

in alcoholic media<sup>9</sup> (product **12** was found later<sup>10</sup> when chloride salts were added to the system prior to irradiation). This diversity of primary reaction pathways, previously unknown in dienone photochemistry, provided us with a simple, sensitive means of evaluating the effect of changes of reaction variables merely by measuring (usually by gas-liquid chromatography) the changes in product distribution. The variables have been found to include the solvent, dienone concentration, light intensity, temperature, and the presence of reagents which can act as sensitizers or quenchers, including oxygen.<sup>4,5</sup> The photochemical pathways observed starting with **7** are summarized in Scheme II and will now be discussed in detail.

### Mechanism of the Radical Fragmentation Reaction

Formation of *p*-cresol (**8**) from irradiation of **7** was originally thought<sup>7</sup> to occur by expulsion of -CCl<sub>3</sub> to give an intermediate phenoxy radical. Subsequent observation that the fragmentation occurred only in solvents which are good H donors toward free radicals suggested a more likely route in which H abstraction of the triplet excited states gives a ketyl radical, **13**, which then expels trichloromethyl radical.<sup>4</sup> This reaction could be triplet sensitized and was quenchable by standard triplet quenchers.<sup>4</sup> The Stern-Volmer slopes led to a rate constant for H abstraction of  $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>4</sup> considerably larger than values derived for H abstraction by standard  $n, \pi^*$  triplets such as benzophenone ( $k_{\text{abs}} \sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>11</sup> and more typical of values determined for intramolecular  $\gamma$  H abstraction in the Norrish II reaction ( $k_{\text{abs}} \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>12</sup>

Subsequent quantitative studies of *p*-cresol (**8**) formation in 2-propanol (IPA), a standard H-donor solvent, gave unusual and initially puzzling results.<sup>5,13</sup> The effect of added 1,3-cyclohexadiene (CHD) on the yields of **8** and ether **10c** is illustrated in Figure 1. This unusual quenching response, noted by two different investigators using different batches of highly purified chemicals,<sup>13</sup> was also observed with piperylene (1,3-pentadiene) and di-*tert*-butyl nitroxide (DTBN) as quenchers. In IPA containing LiCl, the yield of **12** was affected by these quenchers similarly to that of **10c**.<sup>13a</sup>

(9) D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **90**, 5137 (1968).

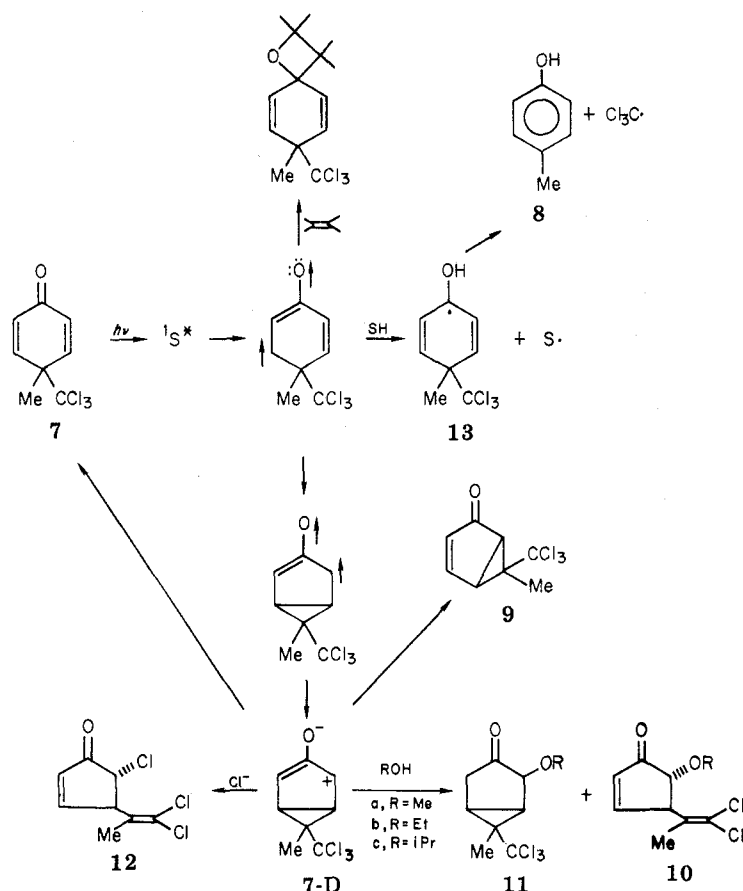
(10) D. I. Schuster and K.-C. Liu, *J. Am. Chem. Soc.*, **93**, 6711 (1971).

(11) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963); M. R. Topp, *Chem. Phys. Lett.*, **32**, 144 (1975), and references cited.

(12) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(13) (a) K.-C. Liu, Ph.D. Dissertation, New York Univ., 1973; (b) G. C. Barile, Ph.D. Dissertation, New York University, 1975.

Scheme II

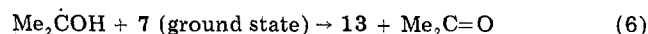
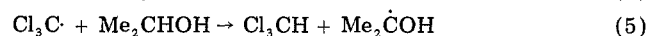
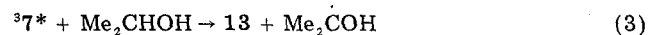


These results indicated that (1) the triplet quenchers are intercepting at least two reaction intermediates and (2) the yield of zwitterion-derived products (see below) in IPA initially increases in the presence of triplet quenchers and then gradually decreases.

A number of recent studies have clarified the mechanistic picture. Acetone and chloroform are formed in IPA in yields nearly identical with that of 8. The quantum efficiency of *p*-cresol formation ( $\Phi_8$ ) is a sensitive function of reaction conditions: (a)  $\Phi_8$  increases as dienone concentration is increased in IPA or ethyl ether; (b)  $\Phi_8$  in IPA is sharply reduced in the presence of  $O_2$  (note that no such effect is observed<sup>4</sup> for  $7 (+h\nu) \rightarrow 9$  in benzene); (c) stirring reduces  $\Phi_8$  in oxygenated IPA; (d)  $\Phi_8$  increases with time in oxygenated IPA, ether, or cyclohexane; (e) in these same oxygenated solvents,  $\Phi_8$  increases as the light intensity  $I_0$  is systematically increased; (f)  $\Phi_8$  decreases with increased  $I_0$  in deoxygenated IPA and ether, but there is no light intensity effect in deoxygenated cyclohexane.

These observations can be understood if a radical-chain process is operating in IPA (Scheme III). A

Scheme III

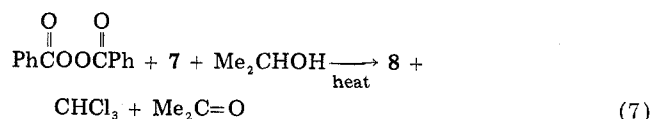


similar scheme can be written for reaction in ethyl ether, where dimerization of ether-derived radicals  $CH_3\dot{C}HOCH_2CH_3$  competes with reaction of the radical with ground-state dienone 7 to give ketyl 13 +

$CH_2=CHOCH_2CH_3$ . In cyclohexane, however, there is no chain reaction, and bicyclohexyl is the only observed solvent-derived product.

Interpreting the curved quenching plot for formation of 8 in IPA (see Figure 1) in terms of the proposed mechanism, we suggest that the dienes and nitroxide intercept one or more radical intermediates in addition to the triplet-state precursor. Similarly, the dramatic effect of oxygen (including the stirring effect) on cresol formation, but not on the lumiketone rearrangement, is directly attributable to interception of a radical intermediate rather than a triplet excited state. Since  $\Phi_8$  increases as the irradiation proceeds, i.e., as  $O_2$  is consumed, radical scavenging must be irreversible.

A test of the proposed mechanism was conceived based on the idea that thermal generation of a proposed chain-carrying radical in the presence of dienone 7 should afford the same final products as observed in the photochemical reactions.<sup>13b,14</sup> For example, thermal decomposition of a radical initiator in IPA would give  $Me_2\dot{C}OH$  radicals, which can initiate the radical chain in Scheme III by reacting with 7 (eq 6). Thermolysis of benzoyl peroxide (BP) at 80 °C in IPA containing 7 indeed afforded *p*-cresol (8) and  $CHCl_3$  in good yields (eq 7). As anticipated, these products were also ob-



served in ethyl ether but not in cyclohexane.

(14) For some related studies, see E. Huyser and K. Johnson, *J. Org. Chem.*, **33**, 3645 (1968).

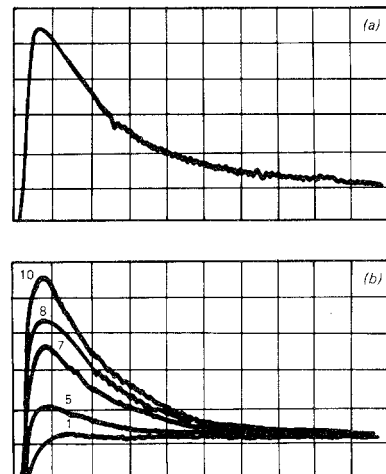
The proposal that triplet quenchers were functioning as free-radical scavengers in these photoreactions was tested by generating  $\text{Me}_2\dot{\text{C}}\text{OH}$  thermally, by decomposition of BP in the presence of **7** and typical "triplet" quenchers. Indeed, both CHD and naphthalene were observed to reduce the yields of **8**.<sup>13b</sup>

The initial increase in the yields of zwitterion-derived products **10c** and **12** that is observed in the photochemical reactions when dienes or nitroxide were added (see Figure 1) can be understood if radicals which would otherwise react with **10c** and **12** are being scavenged. This was confirmed, since thermal decomposition of BP in IPA containing **7** and added **10c** (the control involved heating a similar solution lacking BP) led to consumption of **10c**.

The unusual light intensity effects are also consistent with the radical chain mechanism, involving competition between radical-radical and radical-molecule reactions.<sup>15,16</sup> The arguments are given in a recent paper<sup>5</sup> and will not be repeated here.

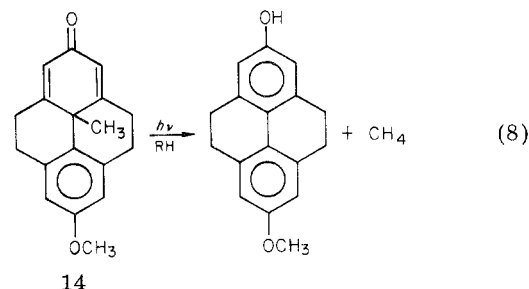
A final series of experiments dramatically confirms many of the above postulates. A number of years ago, attempts were made to detect photochemical transients from several cyclohexadienones including **7** using microsecond as well as nanosecond flash techniques, with a conspicuous lack of success.<sup>17</sup> It therefore came as a surprise when a long-lived transient which decayed by first-order kinetics with a lifetime of  $\sim 200 \mu\text{s}$  was reproducibly observed when **7** was flashed in degassed IPA, ethyl ether, or cyclohexane, but not in benzene,  $\text{CCl}_4$ , or *t*-BuOH.<sup>13,18</sup> The absorption spectrum of the transient has maxima at 540 and 580 nm, and is assigned to ketyl radical **13** by comparison with the spectrum of the parent cyclohexadienyl radical.<sup>19</sup> Studies of the effect of quenchers on the transient intensity and decay rate allow distinction between direct interception of **13** or of a precursor to **13**. It was found that  $\text{O}_2$  and DTBN intercept **13** as well as a precursor (presumably the dienone triplet), while CHD only intercepts the precursor. A plot of transient absorption intensity vs. CHD concentration gives a straight line whose slope is in general agreement with the limiting slope observed in Figure 1, previously<sup>5,13</sup> attributed to triplet quenching. When solutions containing sufficient  $\text{O}_2$  or DTBN to eliminate transient absorption are repeatedly flashed, the absorption gradually returns to its full intensity (Figure 2), demonstrating the irreversible consumption of these quenchers.<sup>18</sup>

The fact that *p*-cresol (**8**) is formed from **7** by a radical chain process of presently unknown chain length in 2-propanol and ethyl ether implies that  $\Phi_S$  can not be equated to the quantum efficiency of H abstraction in these solvents, thereby invalidating the previously assigned rate constant for this process in ethyl ether.<sup>4</sup> These studies unequivocally establish the free-radical character of the lowest dienone triplet state, at least in the case of **7**, and demonstrate the importance of radical fragmentation reactions when dienones with appropriate  $\text{C}_4$  substituents are irradiated in H-donor sol-



**Figure 2.** (a) Decay of transient absorption at 580 nm from flash excitation of 0.1 M dienone **7** in degassed cyclohexane. Time scale  $50 \mu\text{s}/\text{cm}$ . (b) Same as in (a) after addition of  $2 \mu\text{L}$  of DTBN to 70 mL of solution, as a function of total number of flashes. (Reprinted with permission from D. I. Schuster, *Tetrahedron Lett.*, 3017 (1976). Copyright 1976 Pergamon Press.)

vents. That this is not a strict requirement is shown by the behavior of **14**, where the leaving group appears to be a methyl radical (eq 8).<sup>20</sup>



### Evidence for Zwitterion Intermediates

It is informative to recall the original basis for postulating the intermediacy of zwitterions in the dienone-lumiketone photorearrangement.<sup>2a,3</sup> It was recognized that at some critical juncture along the reaction pathway a rearrangement occurred, formally analogous to the reversible cyclopropylcarbinyl-allylcarbinyl "carbonium ion" rearrangements extensively investigated in prior years by Roberts and co-workers.<sup>21</sup> In general, deep-seated structural rearrangements were well established in carbocation chemistry, but were and continue to be virtually unknown in free-radical chemistry,<sup>22,23</sup> although cyclopropylcarbinyl-allylcarbinyl free-radical interconversions had been demonstrated.<sup>24</sup> However, the proper analogy for an electronic excited state and derived intermediates is not a monoradical but a biradical, where the driving force

(20) H. E. Zimmerman and G. Jones, II, *J. Am. Chem. Soc.*, **91**, 5678 (1969); **92**, 2753 (1970).

(21) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961); M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961), and earlier papers.

(22) P. de Mayo, Ed., "Molecular Rearrangements", Part One, Interscience-Wiley, New York, N.Y., 1963, especially Chapters 1, 3, 4, and 7.

(23) C. Walling, in ref 22, Chapter 7.

(24) D. I. Schuster, Ph.D. Dissertation, California Institute of Technology, 1961; R. Breslow in ref 22, p 289 ff; for later studies see T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 3051 (1967), and L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934, 3050 (1967).

(15) H. S. Johnston and F. Cramarossa, *Adv. Photochem.*, **4**, 1 (1966).

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 450 ff.

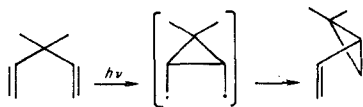
(17) D. I. Schuster and N. K. Lau, *Mol. Photochem.*, **1**, 415 (1969).

(18) D. I. Schuster and G. C. Barile, *Tetrahedron Lett.*, 3017 (1976).

(19) J. E. Jordan, D. W. Pratt, and D. E. Wood, *J. Am. Chem. Soc.*, **96**, 5588 (1974).

for [1,2]alkyl and -hydrogen shifts is very great.<sup>6b,25</sup>

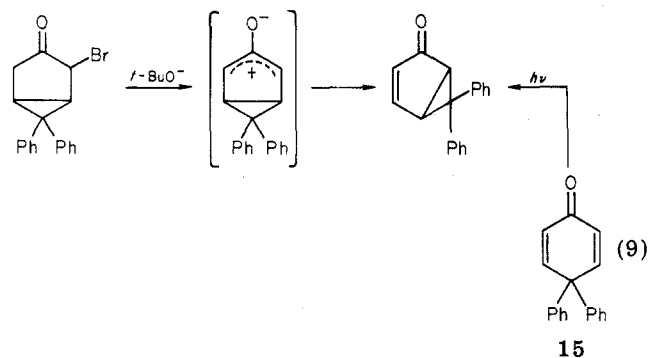
For example, the subsequently well-studied photochemical di- $\pi$ -methane arrangement<sup>26</sup> involves in a key step the rearrangement shown below of a proposed



biradical intermediate or transition state (singlet or triplet), in a manner totally analogous to the direct rearrangement of the bridged intermediate C to the lumiketone product. More recently, the dienone-lumiketone photorearrangement was recognized as a member of the large class of pericyclic reactions characteristic of many neutral, electron-deficient, electron-rich, and radicaloid species which can be generated by either thermal or photochemical initiation.<sup>27</sup>

Theoretically, the oxyallyl diradical species C, with five  $\pi$ -electrons and one unpaired electron in a nonbonding orbital on oxygen, is an  $n, \pi^*$  electronic excited state of zwitterion D, which has four  $\pi$ -electrons and a paired set of nonbonding electrons. The mechanistic question is one of some subtlety, namely whether these molecular rearrangements occur directly from the excited state C or after deactivation to the ground-state D. Conceivably, the problem might be resolvable on the basis of theoretically calculated potential surfaces and correlation diagrams. However, the basic question of concern here is the following: what if any is the experimental evidence which supports (or conceivably contradicts) the originally proposed and apparently generally accepted zwitterion mechanism?

A *prima facie* case has been built by Zimmerman,<sup>28</sup> based on studies where zwitterions analogous to D as generated by *ground-state* reactions indeed afforded lumiketones, as in eq 9. This establishes that such



ground-state species do indeed undergo the rearrangement proposed in Scheme I. However, one can not conclude from such experiments that these zwitterionic species are necessarily the intermediates responsible for the rearrangement in the photochemical

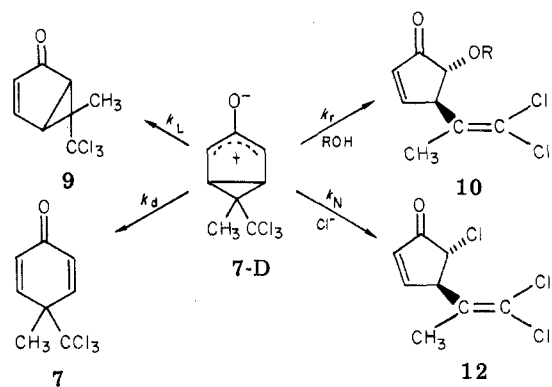
(25) For examples, see G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(26) For a review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(27) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie-Academic Press, 1970, Chapters 6 and 7.

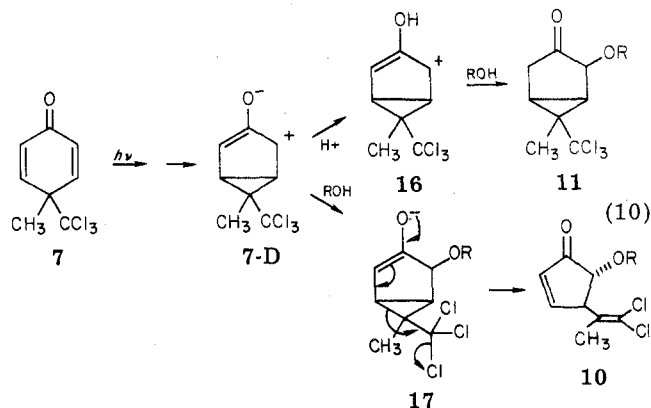
(28) (a) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **91**, 434 (1969); (b) H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 7806 (1972).

Scheme IV



system. Indeed, one might note the possible differences between the intermediate as generated in the Favorskii-type reaction (eq 9) and the proposed photochemical intermediate D with respect to the role of the halide counterion, the degree of vibrational excitation, the precise sequence of bond making and bond breaking, etc. While Zimmerman's studies<sup>28</sup> enhance the plausibility of zwitterion intermediates in the photochemical system, they do not rule out other equally plausible alternatives, such as diradical intermediates.

The only *direct* evidence of which we are aware that zwitterions *must* definitely be involved in these photorearrangements comes from the studies with dienone 7 and related compounds. The formation of products 10 and 11 in alcoholic media is best understood in terms of nucleophilic trapping of 7-D (eq 10).<sup>4</sup> Thus, in acidic

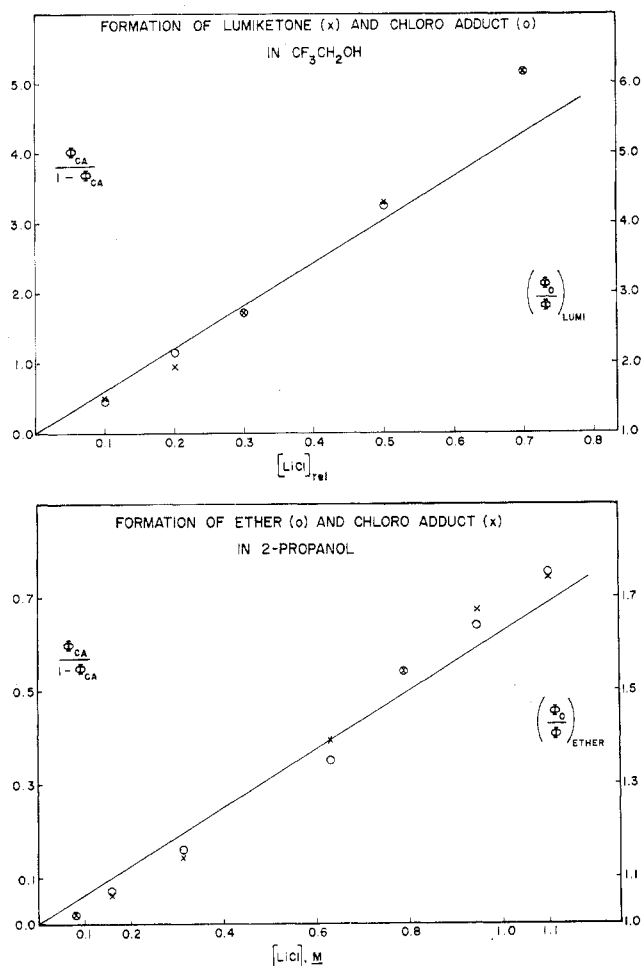


methanol, 7-D is protonated to give the hydroxyallyl intermediate 16, which is captured by methanol to give 11, the unique example of a dienone photoproduct in which the postulated zwitterion structure has been preserved.<sup>29</sup> In the absence of an appropriate electrophile, 7-D is attacked nucleophilically by the alcohol to give 17, which undergoes a Grob-type anionic fragmentation to 10. The *trans* stereochemistry established for 10<sup>4,30</sup> indicates that the nucleophile attacks the five-membered ring as expected from the side opposite to the cyclopropane bridge.

Nucleophiles other than the solvent can capture 7-D, such as halide ions.<sup>10</sup> Thus, in methanol containing LiCl, the formation of product 12 occurred at the expense of product 10a, the ratio of 12/10a increasing linearly as the LiCl concentration was increased.<sup>10,13a</sup>

(29) D. I. Schuster and V. Y. Abraitys, *Chem. Commun.*, 419 (1969).

(30) A. B. Gupta, Ph.D. Dissertation, New York University, 1975.



**Figure 3.** Effect of added LiCl on yields of lumiketone **9** in TFE and methyl ether **10** in IPA (right ordinate), and on the yield of chloride adduct (CA) **12** (left ordinate), as per eq 11 and 12. The value of  $\Phi_Z$  is taken as 1.0. (Reprinted with permission from ref 13a.)

If 7-D is a direct precursor of lumiketone **9**, the yield of **9** should also decrease in the presence of chloride salts, as was indeed observed on photolysis of **7** in 2,2,2-trifluoroethanol (TFE), concomitant with the formation of chloro ketone **12**.<sup>10,13a</sup> Based on a kinetic scheme (Scheme IV) in which 7-D is a common precursor of alkoxy ketone **10**, lumiketone **9** and chloro ketone **12**, kinetic expressions (eq 11–12) can be

$$(\Phi^o/\Phi)_9 = (\Phi^o/\Phi)_{10} = 1 + k_N\tau_Z[Cl^-] \quad (11)$$

$$\Phi_{12}/(\Phi_Z - \Phi_{12}) = k_N\tau_Z[Cl^-] \quad (12)$$

derived<sup>13a</sup> for the yields of these products as a function of  $Cl^-$  concentration, where  $(\Phi^o/\Phi)_i$  is the relative yield of product *i* in the absence and presence of the halide salt,  $\Phi_Z$  is the quantum efficiency of formation of zwitterion 7-D,  $\tau_Z$  is the zwitterion lifetime in the absence of added salts ( $\tau_Z^{-1} = k_1 + k_r[ROH] + k_d$ ), and  $k_N$  is the second-order rate constant for attack of  $Cl^-$  on 7-D. Quantum yields in TFE and methanol and the absence of free-radical products indicate that  $\Phi_Z$  in these solvents must be close to unity. Plots of the measured quantities on the left side of eq 11–12 vs.  $[LiCl]$  were straight lines with a common slope =  $k_N\tau_Z$ , as illustrated in Figure 3.<sup>10,13</sup> These results establish the presence of a common intermediate in these reactions, and it is difficult if not impossible to conceive of an alternative to zwitterion 7-D for this role.

Recent experiments (K. Smith, unpublished) indicate that the counterion also plays a role. Yields of chloro ketone **12** in various solvents are higher using LiCl than NaCl or KCl (at comparable concentrations), indicating that coordination of the metal ion to oxygen is important, and probably facilitates nucleophilic attack at the cationic site. Studies using crown ethers to increase salt solubility in the organic solvents used in these reactions support this hypothesis.

As discussed earlier, irradiation of **7** in IPA gives *p*-cresol (**8**) by radical fragmentation competitive with formation of **10c** by the ionic route. In this system LiCl had only a minuscule effect on the yield of **8**, while the yield of **10c** was sharply reduced,<sup>13</sup> proving that the dienone triplet excited state and zwitterion 7-D are formed sequentially, the former leading to **8** (see above) via intermediates which are not quenchable by  $Cl^-$ . Since triplet quenching experiments (see below) establish that all products of dienone **7** are derived from a triplet excited state, these studies provide experimental confirmation for the sequence of intermediates first postulated in 1961.<sup>3</sup>

The total yield of **9** + **12** in TFE containing LiCl was substantially higher than that of **9** alone in the absence of added salt, the discrepancy being greater at 38 °C than at 0 °C.<sup>13a</sup> There must therefore be an additional temperature-dependent process which consumes 7-D in TFE, but this cannot involve formation of ethers **10** and **11** which are at best minor products according to GLC and NMR data. We suggest that this additional zwitterionic reaction is the reversion of 7-D to ground-state dienone **7**. This electrocyclic ring opening is formally forbidden on the basis of orbital symmetry considerations,<sup>27</sup> and a high activation barrier is therefore anticipated. Zimmerman and Swenton<sup>31</sup> have shown that such zwitterions correlate with a doubly excited state of the corresponding dienone. We believe that such reversion is nonetheless responsible for the residual quantum inefficiency on photoexcitation of cyclohexadienones, and we predict that this source of inefficiency should become more important as the temperature is raised.<sup>32</sup> This has not yet been evaluated experimentally.

Addition of LiCl had absolutely no effect on the efficiency of lumiketone formation on irradiation of santonin (**1**) or dienone **15** in TFE, and no new products were observed.<sup>10,13a</sup> This requires that either (a) zwitterions are not reaction intermediates in these systems, or (b) zwitterions are indeed involved, but their lifetimes are much shorter than that of 7-D. We favor explanation b. Since the only primary reaction occurring on photolysis of **1** and **15** is lumiketone formation,<sup>1–3</sup> zwitterions in these cases have only two options, decay to ground-state dienone and [1,4]sigmatropic rearrangement. Given the high quantum efficiencies for lumiketone formation ( $\sim 0.85$ ),<sup>31,33</sup> it is evident that  $\tau_Z$  is determined principally by  $k_L$  (see Scheme IV). Since positive charge is largely localized at C<sub>6</sub> in the transition state of the [1,4] rearrangement,<sup>32</sup> the electron-withdrawing CCl<sub>3</sub> group in **7** strongly inhibits this reaction (increasing  $E_{act}$ , decreasing  $k_L$ ) while alkyl and aryl groups in **1** and **15** enhance  $k_L$  and de-

(31) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

(32) D. I. Schuster, *Pure Appl. Chem.*, **41**, 601 (1975).

(33) D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968).

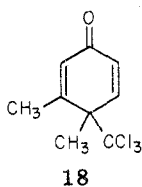
crease  $\tau_z$ . Thus, inclusion of the  $\text{CCl}_3$  moiety in the dienone system for another mechanistic purpose (see above) fortuitously made the derived zwitterion amenable to trapping and kinetic study, which has not been possible in other dienone systems studied to date.

Irradiation of santonin (1), lumisantonin (2), and some  $\alpha$ -halo derivatives in glasses or polystyrene at 77 K has been reported to give blue transient intermediates which are not paramagnetic, and which are thought to be the corresponding zwitterions.<sup>34</sup> Since these species could not be trapped, this assignment must be considered tentative. Interestingly, we have also seen a blue color on irradiation of 7 at low temperatures in glasses. Further spectroscopic studies at low temperature are clearly required to substantiate these observations, to provide a definite assignment of structure to the "blue intermediate", and to provide a link between the spectroscopic observations at low temperature and the photochemical behavior at ambient temperatures.

In summary, the zwitterion mechanism for the cyclohexadienone photorearrangement at ambient temperatures has a solid basis in experimental fact only from the studies on 7.<sup>4,10,13</sup> Extension to other dienones rests entirely on the principle of analogy and our penchant for mechanistic simplicity, supported by prima facie evidence from related ground-state reactions.<sup>28</sup>

### Stereochemistry of the Dienone-Lumiketone Photorearrangement

We recognized some years ago, simultaneously with Woodward and Hoffmann,<sup>35</sup> that determination of the absolute stereochemistry of the photochemical rearrangement of an unconstrained monocyclic 2,5-cyclohexadienone to its corresponding lumiketone(s) would provide considerable insight into the electronic structure of the intermediates involved in this transformation, as well as the molecular gyrations occurring at each step. Previous studies had been confined to steroidal dienones in which the constraints of the fused-ring systems might have prejudiced the outcome.<sup>36</sup> Our studies using the chiral dienone 18,<sup>37</sup>



which require correlation of the absolute configurations of the starting optically active dienone and the (two) diastereomeric optically active lumiketones, gave an ambiguous result. Thus, detailed discussion of this aspect of the problem would be premature at this time. We fully expect that this ambiguity will be resolved satisfactorily in the very near future.

### Multiplicity, Configuration, and Energy of Reactive Excited States

At the time Scheme I was proposed,<sup>2a,3</sup> the multiplicity of the excited state(s) responsible for photochemical reactions of cyclohexadienones had not been established. Soon afterward, application of the triplet sensitization techniques developed in Hammond's laboratory to santonin (1)<sup>38</sup> and dienone 15<sup>31</sup> showed that the quantum yields for lumiketone formation on benzophenone ( $E_T = 68.5$  kcal/mol) or acetophenone ( $E_T = 73.6$ ) sensitization<sup>39</sup> were the same as on direct irradiation of the dienones ( $\sim 0.85$ ).<sup>38</sup> These results suggest, but do not require, that the reactive excited state in the direct photolysis is a triplet, and that the singlet to triplet intersystem crossing efficiency is unity. However, triplet quenching results were inconclusive. Naphthalene ( $E_T = 61$ ) did not quench the isomerization of 15;<sup>31</sup> quenching of the isomerization of 1 by neat piperylene (1,3-pentadiene) was observed, but 1 did not sensitize the cis-trans isomerization of piperylene ( $E_T = 57-59$ ) in dilute solution,<sup>38</sup> as would have been anticipated.

The situation was somewhat clarified by studies in our laboratory, using a sensitive GLC analytical method, which showed that: (a) the photoisomerization of 15 was quenchable by piperylene<sup>16</sup> and even more efficiently by 1,3-cyclohexadiene (CHD) ( $E_T = 53$ );<sup>40</sup> (b) the photoisomerization of 1 was quenched inefficiently by dienes, the most effective being CHD;<sup>16,40</sup> (c) the quenching of 1 by CHD in high concentration involves exclusively transfer of triplet excitation, as determined by a "triplet counting" technique in which the yield of CHD dimers was correlated with the reduction in yield of 2;<sup>33</sup> (d) triplets derived from nine dienones are quenched with markedly different efficiencies by piperylene and CHD, the quenching ratio varying from 1.5 to 15;<sup>40</sup> (e) the quenching of 7 by CHD in benzene had a Stern-Volmer slope independent of dienone concentration,<sup>13a</sup> establishing that reversible energy transfer is not important in this system.

These data and the complementary sensitization results establish that these dienone reactions derive from a triplet excited state. The lifetime of such triplets is more problematical. If quenching by CHD occurs at a diffusion-limiting rate ( $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in benzene),<sup>39,41</sup> the limits on  $\tau_T$  for the dienones are  $1.5 \times 10^{-9}$  s (7) and  $4 \times 10^{-11}$  s (1). The conclusion that triplet lifetimes in these systems are as short or shorter than characteristic singlet excited-state lifetimes is unusual but not absurd, since the triplet decay is governed by unimolecular reaction modes whose rate constant could conceivably be on the order of  $10^{10}$  or  $10^{11} \text{ s}^{-1}$ .

However, the assumption that triplet quenching by CHD is diffusion limited must first be examined. Although CHD was the best quencher of those we examined, this is no assurance that a better quencher might not be discovered which has a larger  $k_q\tau_T$  corresponding to a longer  $\tau_T$ . The lowest triplet states of

(34) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **90**, 1547 (1968); M. H. Fisch, *Chem. Commun.*, 1472 (1969).

(35) Reference 27, p 89 ff.

(36) F. Frei, C. Ganter, K. Kagi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

(37) D. I. Schuster and K. V. Prabhu, *J. Am. Chem. Soc.*, **96**, 3511 (1974); D. I. Schuster, K. V. Prabhu, S. Adcock, J. Van der Veen, and H. Fujiwara, *J. Am. Chem. Soc.*, **93**, 1557 (1971); K. V. Prabhu, Ph.D. Dissertation, New York University, 1972; D. I. Schuster, K. V. Prabhu, and J. van der Veen, unpublished results.

(38) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963).

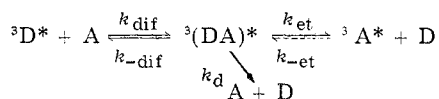
(39) For a review of the literature on triplet energy transfer and tables of triplet excitation energies, see A. A. Lamola, in "Energy Transfer and Organic Photochemistry", "Technique of Organic Chemistry", A. Weissberger and P. A. Leermakers, Ed., Interscience-Wiley, 1969.

(40) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *J. Am. Chem. Soc.*, **90**, 5027 (1968).

(41) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966); W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969).

1, 7, and 15 have been placed at  $68 \pm 1$  kcal above the respective ground states, based on low-temperature phosphorescence in glasses,<sup>4,31,38</sup> in which case transfer of triplet excitation to CHD ( $E_T = 53$ ) ought to be diffusion controlled.<sup>39,42</sup> However, it is then difficult to understand why triplet transfer from the dienones to piperylene and naphthalene ( $E_T$  59 and 61, respectively) does not occur at this same diffusion-controlled rate. There would appear to be two possibilities: (a) some factor other than the difference in donor and acceptor triplet energies is diminishing  $k_q$ , or (b) the effective triplet energies of the dienones in solution at room temperature are much less than the values derived from low-temperature phosphorescence emission. If triplet-energy transfer involves a triplet exciplex  ${}^3(\text{DA})^*$  intermediate which can partition between reversion to donor triplets, decay to two ground states, and formation of acceptor triplets (Scheme V), the rate constant for energy transfer  $k_q$  is then given by eq 13.<sup>32,43-45</sup>

Scheme V



$$k_q = k_{dif}k_{et}(k_{et} + k_d + k_{-dif})^{-1} \quad (13)$$

Since the factors which govern the partitioning exciplexes have yet to be established, this process could conceivably be important for the dienones.

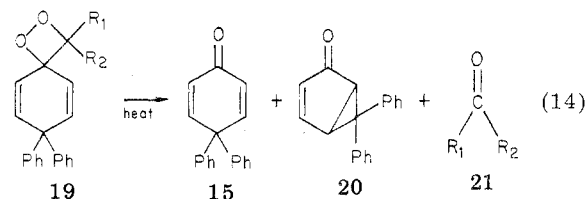
Alternatively, spectroscopic dienone triplets may rapidly relax in solution (precluding interception) to a lower energy form whose geometry is different from that of the ground state. Rates of quenching of the relaxed triplet by naphthalene and the dienes may be much less than diffusion limited.<sup>39</sup> Such a possibility has not been excluded by the available data and is in fact quite plausible. The bridged triplet C in Scheme I, whose value of  $E_T$  may be much lower than that of B, could be the species actually intercepted by the prospective quenchers. Studies with very low energy triplet quenchers are required to assess this possibility.

The original mechanistic postulate of 1961 (Scheme I) was predicated on an  $n, \pi^*$  state as the reactive excited species.<sup>2a,3</sup> The weak long-wavelength UV absorption of 2,5-cyclohexadienones involves excitation to a singlet  $n, \pi^*$  state ( $S_1$ ). Since the photochemistry arises from a triplet state, this could be either  ${}^3n, \pi^*$  or  ${}^3\pi, \pi^*$ , which both lie below  $S_1$ . In the cases of 7, 15, and some other monocyclic dienones, the phosphorescence at 77 K in glasses seems to originate from a  ${}^3n, \pi^*$  state,<sup>4,31,46</sup> based on the pronounced vibronic splitting, effects of solvent polarity on emission wavelength, the direction of emission polarization, and the short emission lifetime. However, from analogous studies of santonin (1) and some analogues<sup>47</sup> which also incor-

porated phosphorescence excitation measurements at 4.2 K and investigation of heavy atom effects, phosphorescence was assigned to a  ${}^3\pi, \pi^*$  state lying below the  ${}^3n, \pi^*$  state. Strong vibronic interaction between the two states was postulated. Our results on 18,<sup>36</sup> which appears to have a lowest  ${}^3\pi, \pi^*$  state, indicate that introduction of only one methyl group can invert the order of the triplet states.

When two triplet states are energetically proximate, thermal population of a reactive  $T_2$  state from an unreactive  $T_1$  state at ambient temperatures can occur, a phenomenon which has been demonstrated in other systems.<sup>48</sup> A pronounced temperature dependence of the photochemistry should ensue, an effect yet to be investigated in dienone photochemistry. It was suggested some time ago<sup>38</sup> that the photochemistry of santonin originated from a  ${}^3\pi, \pi^*$  state, supported by results of the later spectroscopic investigations,<sup>47</sup> but reaction from an upper  ${}^3n, \pi^*$  state is a distinct possibility in this system. Recent quenching studies on 18<sup>36</sup> led us to question the role of  ${}^3n, \pi^*$  states in photoisomerization, since it appeared that two triplets were active in this system, one responsible for H abstraction and another for isomerization. However, an alternative explanation for the observations later became apparent,<sup>5</sup> involving quenching of radicals as well as triplets in the abstraction reaction, which permits the viability of isomerization directly from the  ${}^3n, \pi^*$  state.

Zimmerman and co-workers<sup>49</sup> very recently studied the generation of excited states of dienone 15 by thermal decomposition of dioxetanes 19 (eq 14). From



previous studies with acetone and other alkanones,<sup>50</sup> such reactions should generate triplet excited states of either dienone 15 or the accompanying ketone 21, depending on which has the lower triplet energy. Theoretical considerations<sup>51</sup> have led others to conclude that the formation of  $n, \pi^*$  triplets should be kinetically preferred over  $\pi, \pi^*$  triplets. Starting with five different dioxetanes 19, the lumiketone 20 derived from dienone 15 was indeed formed in substantial yields.<sup>49</sup> In four cases, the alternative product (21) has a higher triplet energy than 15, but the reaction course was not altered in the fifth case where the product 21 was 2-acetonaphthone. The authors argue that this shows that the higher energy  $n, \pi^*$  triplet of 15 ( $E_T = 68.5$  kcal/mol) is formed preferentially to the lower energy  $\pi, \pi^*$  triplet of 2-acetonaphthone ( $E_T = 59$  kcal/mol),<sup>49</sup> thereby

(47) G. Marsh, D. R. Kearns and M. Fisch, *J. Am. Chem. Soc.*, **92**, 2252 (1970).

(48) P. J. Wagner, A. E. Kemppainen, and A. N. Schott, *J. Am. Chem. Soc.*, **92**, 5280 (1970); **95**, 5604 (1973); P. J. Wagner and J. Nakahira, *ibid.*, **95**, 8474 (1973).

(49) H. E. Zimmerman, G. E. Keck, and J. L. Pfloderer, *J. Am. Chem. Soc.*, **98**, 5574 (1976).

(50) For a review, see N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974); see also E. J. H. Bechara, A. L. Baumstark, and T. Wilson, *J. Am. Chem. Soc.*, **98**, 4648 (1976).

(51) D. R. Kearns, *Chem. Rev.*, **71**, 345 (1971); N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 3589 (1975), and references cited.

(42) H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); **14**, 48 (1960); G. Porter and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, **264**, 1 (1961); W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(43) A. Gupta and G. S. Hammond, *J. Chem. Phys.*, **57**, 1789 (1972).

(44) M. A. Schexnayder and P. S. Engel, *Tetrahedron Lett.*, 1153 (1975).

(45) M. W. Wolf, R. E. Brown, and L. A. Singer, *J. Am. Chem. Soc.*, **99**, 526 (1977).

(46) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Am. Chem. Soc.*, **89**, 6589 (1967).



proving the configuration of the lowest triplet of **15** in solution at ambient temperature. There is a fault in this argument, alluded to earlier. If the *effective* triplet energy of **15** is substantially less than the phosphorescence-derived value of 68.5 kcal/mol (as suggested by the otherwise baffling quenching results on these systems), the results could be explained simply on the basis of energy considerations, without injecting the configurational question.

Thus, the situation with respect to characterization and identification of triplet excited states of dienones is perhaps more unsettled than might be gathered from the recent literature. The possibility that reaction occurs in some systems from a thermally populated upper triplet needs to be explicitly evaluated, and there is a need for additional spectroscopic studies of dienones at low temperature and in solution. However, considering all of the data, there is at present no experi-

mental evidence which is *inconsistent* with the original proposal<sup>2a,3</sup> that the photoreactions of 2,5-cyclohexadienones originate exclusively from  $n,\pi^*$  excited states.

*These studies are the fruits of the labor of a steady stream of able and dedicated associates, mostly doctoral candidates, who have contributed significantly to the conceptual as well as the experimental foundation of this research. I acknowledge with pleasure their zeal, perseverance, skill, and (most of the time) good humor. In order of appearance, they are Carl Polowczyk, Ira Krull, Dinshaw Patel, Arthur Fabian, William Curran, William Barringer, Stuart Adcock, Noland Kong, Vasanth Prabhu, Kou-chang Liu, George Barile, Atma Gupta, and Karl Smith. Financial support at various times from the U.S. Army Research Office (Durham) and the National Science Foundation was gratefully received. I am also particularly grateful to K. L., G. B., Jens Eriksen, and Frank Mallory for critical comments on this manuscript, and to my colleagues at NYU for their criticisms, advice, and encouragement.*