

properties. The ring closure process ( $k_{12}$  in Scheme II) to give the internally converted  $S_0^*$  proceeds equally competitively with the decarbonylation process ( $k_{14}$  in Scheme III) in CB and chloro-CB. There appears to be no "heavy atom effect," implying that these processes are much more rapid than the possible spin forbidden intersystem crossing process which might enhance the  $C_3$  product quantum yield. In other words, the "heavy atom enhancement" by Cl atom here is not sufficient to influence the overall "singlet pathway."

There is one difference of importance in the secondary processes the cyclopropanes undergo. Energetically, the hot  $c\text{-C}_3\text{H}_6$  resulting from the  $\text{CB}(S_1^*)$  decomposition should be similar to the  $c\text{-C}_3\text{H}_5\text{Cl}$ , but the Arrhenius parameters for their isomerization to an olefin by 1,2-H migration (for CB)<sup>29</sup> and 1,2-Cl migration or the subsequent HCl elimination (for chloro-CB)<sup>23,30</sup> are very different. The lower activation energy for isomerization to an olefin for  $c\text{-C}_3\text{H}_5\text{Cl}$  (52.6 kcal/mol)<sup>30a</sup> allows it to isomerize more readily than  $c\text{-C}_3\text{H}_6$  (65.6 kcal/mol)<sup>29b</sup> at comparable pressure and photoactivation energy as witnessed in Figures 6 and 7 and Tables II and III. The many isomerization and HCl elimination channels render the energy partitioning study more cumbersome. One could easily

(29) (a) T. C. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934); (b) W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 609 (1961);  $k_{(\text{isomerization})} = 10^{15.45} \exp(-65,600/RT) \text{ sec}^{-1}$  for cyclopropane.

(30) (a) R. C. S. Grant and E. S. Swinbourne, *Chem. Commun.*, 620 (1966); see ref 23  $k$  (isomerization to 3-chloropropene) =  $10^{14.5} \exp(-56,200/RT) \text{ sec}^{-1}$ ; (b) B. C. Young and E. S. Swinbourne, *J. Chem. Soc. B*, 1181 (1967);  $k(-\text{HCl}) = 10^{14.49} \exp(-50,200/RT) \text{ sec}^{-1}$  for 2,2-dichlorobutane.

estimate the value of  $\langle\tau(E)\rangle$  for the hot  $c\text{-C}_3\text{H}_5\text{Cl}$  produced at  $\lambda_{\text{ex}}$  325 and 309 nm to be  $\geq 5$  and  $\geq 2$  nsec, respectively, from Figures 6 and 7. An energy partition study in the future may be worthwhile on the basis of this study.

The fact that  $\tau_S$  of chloro-CB  $\approx 0.4$  nsec compared with  $\tau_S$  of CB  $\approx 4.9$  nsec<sup>31</sup> below their "predissociation" limit could mean that the rate of the  $S_1 \rightarrow T_1$  intersystem crossing may be 10 times faster for chloro-CB( $S_1^*$ ) than that of CB( $S_1^*$ ).

## Appendix

The parameters used to calculate the specific rate constant  $k(E)$  of the processes shown in Table VII, according to the approximate formulation of the RRKM rate theory<sup>31</sup>

$$k(E) = A' \left[ \frac{E - E_0 + a^+ E_z^+}{E + a E_z} \right]^{s-1}$$

are  $s = 27$ ;  $E_z = E_z^+ = 50.2$  kcal/mol estimated from the fundamental vibrational frequencies,<sup>32</sup>  $E_{\text{th}} = 2.2$  kcal/mol;  $a = a^+ = 0.90$ . The Arrhenius parameters for the processes "a"–"d" (see Table VII) are as determined previously.<sup>5</sup>

$$k_a = 1.8 \times 10^{14} \exp[-50,600/RT]$$

$$k_b = 1.6 \times 10^{15} \exp[-55,400/RT]$$

$$k_c = 1.2 \times 10^{14} \exp[-53,400/RT]$$

$$k_d = 4.1 \times 10^{13} \exp[-55,000/RT]$$

(31) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(32) J. R. Durig and W. H. Green, *J. Mol. Spectrosc.*, **27**, 95 (1968).

## A Mechanistic Study of the Quenching of Naphthalene Fluorescence by *cis,trans*-1,3-Cyclooctadiene

Steven L. Murov,\* Loh-sheng Yu, and Linda P. Giering

Contribution from the Department of Chemistry,  
State University of New York at Stony Brook, Stony Brook, New York 11790.  
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**Abstract:** Quenching rates of naphthalene fluorescence have been measured for *cis,trans*-1,3-cyclooctadiene (**1**) and 1,2-dimethylcyclobutene (**2**) and are  $5.0 \times 10^8$  and  $1.7 \times 10^7$  l./mol sec, respectively. For **1**, the quenching leads to isomerization to *cis,cis*-1,3-cyclooctadiene (**4**) and adduct formation with naphthalene with quantum yields of 0.07 and 0.12, respectively. The compound bicyclo[4.2.0]oct-7-ene (**3**) is not formed from **1** despite a low activation energy for this process. For compound **2**, the only result of quenching is a small amount of adduct formation. These observations lead to the conclusion that isomerization in nonclassical singlet quenching systems is a result of bonding changes that occur during the formation of the exciplex.

The observation that dienes and quadricyclene quench the fluorescence of aromatic hydrocarbons despite the fact that the conditions for classical energy transfer are not met has led to several investigations.<sup>1–12</sup>

(1) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

(2) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(3) L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," Taylor and Francis, Ltd., London, 1967, p 35.

(4) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

Most investigators agree that exciplex formation is

(5) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(6) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971)

(7) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(8) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

(9) G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3684 (1972).

(10) G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3687 (1972).

(11) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968).

(12) S. L. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

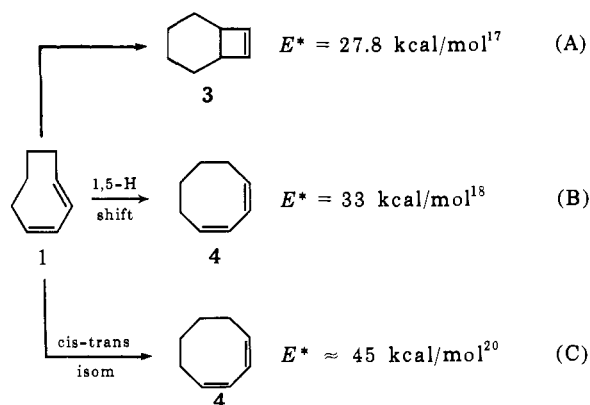
involved in the quenching process. However, the nature of the exciplex and the disposition of its energy are still not completely clear. Several investigators have depicted the exciplex as a charge-transfer complex.<sup>5-7</sup> Hammond and coworkers have suggested that the exciplex should be more realistically formulated as four contributing structures  $D^*Q \leftrightarrow DQ^* \leftrightarrow D^+Q^- \leftrightarrow D^-Q^+$ .<sup>8-10,12</sup> The picture has been complicated by the observations that, as a result of the quenching process, quadricyclene isomerizes with a quantum yield of 0.52 to norbornadiene<sup>12</sup> whereas dienes remain chemically unchanged.<sup>2</sup> The difference occurs despite the observations that the quenching rate constants for quadricyclene and dienes demonstrate similar sensitivities to electronic and structural changes of the aromatic hydrocarbon donor. Two mechanistic views involving either formation or collapse of the exciplex have been advanced to account for the isomerizations. Hammond and coworkers have suggested that vibrational energy which is partitioned to the quencher upon internal conversion of the exciplex can lead to isomerization.<sup>8,10,12,13</sup> The fact that quadricyclene isomerizes and dienes do not as a result of quenching can be attributed to factors governing the energy partitioning process and to the large difference in activation energies for isomerization.<sup>10,14</sup>

It is also possible that isomerization is a result of bonding changes that occur during the formation of the exciplex in order to maximize the binding energy. Steel, *et al.*, suggested that quenching by quadricyclene leads to an exciplex in which the quadricyclene is distorted and has a partial positive charge; collapse of such a species could lead to norbornadiene.<sup>5</sup> For dienes, it is conceivable that exciplex formation does not involve bonding changes in the direction of cis-trans isomerization.

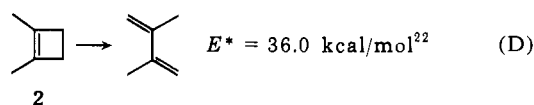
## Results and Discussion

As part of an investigation of the mechanistic questions raised above, we have determined quenching constants of naphthalene fluorescence by *cis,trans*-1,3-cyclooctadiene (**1**) and 1,2-dimethylcyclobutene (**2**) and the resultant chemistry of **1** and **2**. Compound **1** has two isomerization pathways with activation energies lower than that for the quadricyclene to norbornadiene conversion (Scheme I).<sup>15,17,18</sup> The ring opening of

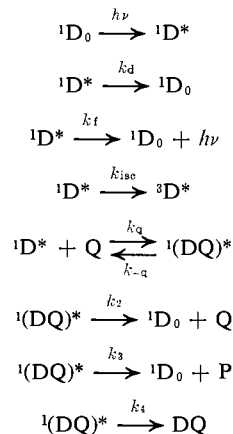
Scheme I



**2** to 2,3-dimethyl-1,3-butadiene also has a low activation energy.<sup>22</sup>



The usual mechanism for fluorescence quenching



where **D** represents the aromatic hydrocarbon, **Q** the quencher,  ${}^1(DQ)^*$  an exciplex, **P** the isomerized **Q**, and **DQ** an adduct of **D** and **Q**, leads to the following Stern-Volmer equation

$$\frac{\Phi_f^0}{\Phi_f} = 1 + k_q \tau_0 [Q] \left( \frac{k_2 + k_3 + k_4}{k_{-q} + k_2 + k_3 + k_4} \right)$$

with  $\tau_0 = 1/(k_d + k_f + k_{isc})$ . The measured quenching constant,  $k_q'$ , then is equal to  $k_q[(k_2 + k_3 + k_4)/(k_{-q} + k_2 + k_3 + k_4)]$ . Values of  $k_q'$  in cyclohexane for **1**, **2**, bicyclo[4.2.0]oct-7-ene (**3**), *cis,cis*-1,3-cyclooctadiene (**4**), and *trans*- and *cis*-cyclooctene, (**5**) and (**6**), respectively, are presented in Table I.

With ionization potentials of **1-6** unavailable, it is not possible to compare the charge-transfer model to our quenching data. However, the strain energy difference measured between **6** and **5** of 9.3 kcal/mol should be reflected in the adiabatic ionization potential. The observations that **5** and **1** quench much faster than **6** and **4**, respectively, could be attributed to the lower ionization potentials. As shown in Table I, compound **2** quenches 1-cyanonaphthalene with a quenching constant of  $1.9 \times 10^8 \text{ l.}/(\text{mol sec})$ . Taylor's results<sup>7</sup> would lead to a prediction of at least  $2 \times 10^9 \text{ l.}/(\text{mol}$

(13) R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2739 (1970).

(14) The activation energies for the quadricyclene to norbornadiene conversion and isomerization of *trans*-1,3-pentadiene to *cis*-1,3-pentadiene have been determined to be 33.5<sup>15</sup> and 52.6<sup>16</sup> kcal/mol, respectively.

(15) H. M. Frey, *J. Chem. Soc.*, 365 (1964).

(16) H. M. Frey, A. M. Lamont, and R. Walsh, *J. Chem. Soc. A*, 2642 (1971).

(17) J. J. Bloomfield and J. S. McConaghy, *Tetrahedron Lett.*, 3723 (1969).

(18) The value for process B has been calculated assuming **3** isomerizes to **4** via **1** from an  $E^*$  for the conversion of **3** to **4** of 38.5 kcal/mol<sup>19</sup> and  $\Delta H$  of 5.6 kcal/mol<sup>17</sup> for the equilibrium  $3 \rightleftharpoons 1$ .

(19) R. Criegee, D. Seebach, R. E. Winter, B. Borretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2338 (1965).

(20) The value has been estimated from the difference between a calculated activation energy, 54.3 kcal/mol,<sup>18</sup> for the isomerization of *trans*-1,3-pentadiene to *cis*-1,3-pentadiene via a biradical mechanism and a strain energy difference between *cis*- and *trans*-cyclooctene of 9.3 kcal/mol.<sup>21</sup> Frey has measured an activation energy of 52.6 kcal/mol for pentadiene isomerization; however, he has proposed that the process proceeds through a cyclobutene intermediate.<sup>16</sup>

(21) R. B. Turner and W. R. Meadow, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(22) H. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963).

**Table I.** Quenching Constants of Naphthalene Fluorescence<sup>a</sup>

Quencher	$10^{-7}k_q', l./(\text{mol sec})^b$
<i>cis,trans</i> -1,3-Cyclooctadiene (1)	50
Bicyclo[4.2.0]oct-7-ene (3)	5.7
<i>trans</i> -Cyclooctene (5)	4.2
1,2-Dimethylcyclobutene (2)	1.7 (19 <sup>d</sup> )
<i>cis,cis</i> -1,3-Cyclooctadiene (4)	0.47
<i>cis</i> -Cyclooctene (6)	0.14

<sup>a</sup> Cyclohexane as solvent. <sup>b</sup> Quenching constants were measured by using the relative intensity method and a single lifetime for naphthalene of 96 nsec. <sup>c</sup> F. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1971, p 330. <sup>d</sup> 1-Cyanonaphthalene as sensitizer.

sec) for this compound. The reason for this discrepancy is not clear to us.

Resultant chemistry for **1** as a consequence of quenching proved to be extremely difficult to ascertain due to two factors. First, thermal dimerization of **1** occurs at room temperature<sup>23</sup> and corrections for the disappearance of **1** obtained from nonirradiated solutions had to be applied to the irradiated solutions. Second, although the irradiations were carried out at concentrations of **1** such that a minimum of 90% of the naphthalene singlet states were quenched, some naphthalene triplets were still produced. Naphthalene triplets sensitize *cis*-*trans* isomerization of **1** to **4**.<sup>24</sup> The quantum yields for the *cis*-*trans* isomerization of **1** sensitized by Michler's ketone and *p*-phenylbenzophenone, both with triplet energies similar to that of naphthalene ( $E_T = 60.9$  kcal/mol),<sup>26</sup> with and without the presence of isoprene were measured. It was found that isoprene and **1** quench triplets of Michler's ketone and *p*-phenylbenzophenone at similar rates. Crude corrections for the isomerization from the triplet state were made by assuming that the portion of naphthalene singlets not quenched by **1** undergo intersystem crossing with a quantum yield 0.8<sup>27</sup> and resultant triplets of **1** isomerize to **4** with a quantum yield of 0.5 (see Table II).

The corrected results are summarized in Table III.

**Table II.** *Cis-Trans* Isomerization of *cis,trans*-1,3-Cyclooctadiene from Triplet State<sup>a</sup>

Sensitizer	$E_T^b$ , kcal/mol	Isoprene,		$\phi_{\text{isom}}^d$
		COD, <sup>c</sup> <i>M</i>	<i>M</i>	
Michler's ketone	61	0.119		0.44
		0.397		0.56
		0.445		0.44
		0.362	0.435	0.24
<i>p</i> -Phenylbenzophenone	60.7	0.138		0.54
		0.445		0.50
		0.362	0.435	0.26

<sup>a</sup> The concentrations for Michler's ketone and *p*-phenylbenzophenone in benzene were about  $10^{-3}$  *M*. Solutions were irradiated at 313 nm at room temperature. <sup>b</sup> See ref 26. <sup>c</sup> COD represents *cis,trans*-1,3-cyclooctadiene. <sup>d</sup> Quantum yields for *cis*-*trans* isomerization of COD to yield **4**.

(23) A. Padwa, W. Koehn, V. Masaracchia, C. L. Osborn, and P. J. Trecker, *J. Amer. Chem. Soc.*, **93**, 3633 (1971).

(24) This conclusion can be deduced from the results of Liu<sup>25</sup> and our own observations in Table II.

(25) R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).

(26) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, N. Y., in press.

(27) A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **306**, 257 (1968).

**Table III.** Singlet Quenching Study of Naphthalene by *cis,trans*-1,3-Cyclooctadiene<sup>a</sup>

COD, <i>M</i>	Naph, <i>M</i>	Other dienes,				
		<i>M</i>	$\phi_{\text{-naph}}^b$	$\phi_{\text{isom}}^c$	$\phi_{\text{isom}}^d$	
0.397	0.200		0.10	0.081	0.066	0.069
0.504	0.200		0.12	0.082	0.070	0.073
0.647	0.200		0.12	0.088	0.079	0.082
0.696	0.193		0.13	0.094	0.085	0.088
0.854	0.199		0.12	0.055	0.047	0.048
0.994	0.200		0.13	0.077	0.071	0.072
2.027	0.200		0.14	0.084	0.081	0.082
4.011	0.200		0.15	0.048	0.046	0.046
0.397	0.117		0.10	0.072	0.057	0.060
0.397	0.200		0.10	0.081	0.066	0.069
0.397	0.401		0.12	0.088	0.073	0.077
0.397	0.599		0.12	0.084	0.069	0.073
		Isoprene				
0.397	0.200	0	0.10	0.081	0.066	0.069
0.397	0.200	0.451	0.12	0.077	0.064	0.070
0.397	0.200	0.763	0.11	0.061	0.054	0.061
0.397	0.200	1.388	0.12	0.056	0.052	0.063
		DMHD <sup>f</sup>				
0.593	0.200	0.521	0.15	0.019		

<sup>a</sup> Cyclohexane as solvent, solutions were irradiated at 313 nm at room temperature. <sup>b</sup> Quantum yields for naphthalene disappearance. <sup>c</sup> Observed quantum yields for *cis*-*trans* isomerization from **1** to **4**. <sup>d</sup> Quantum yields for isomerization after corrections were made for the triplet state. <sup>e</sup> Quantum yields for isomerization after adjusting values from *c* to complete fluorescence quenching. <sup>f</sup> DMHD represents 2,5-dimethyl-2,4-hexadiene.

Three conclusions regarding **1** can be made. First, it should be noted that formation of **3** could not be detected, *i.e.*, process A does not occur ( $\phi < 0.01$ ). Hence, if the activation energy is an important quantity in determining reactivity, it is not the only limiting factor. Second, naphthalene-diene exciplexes, besides collapsing to naphthalene and diene, can form adducts. For **1**, the quantum yield of adduct formation corrected to total fluorescence quenching is 0.12, and this yield is independent of the concentrations of **1** and naphthalene. We have collected three naphthalene-**1** adducts by glc and verified their 1:1 nature by nmr and mass spectrometry, but structure determinations have not been made. The singlet nature of the adduct formation has been verified by the observation that the addition of isoprene, a poor singlet quencher ( $k_q = 1.8 \times 10^7$  l./mol sec)<sup>9</sup> but an efficient quencher of naphthalene triplets ( $k_q = 4 \times 10^8$  l./mol sec),<sup>28</sup> to the system does not affect the quantum yield of adduct formation. These results are consistent with a previous report that naphthalene and butadiene form photochemical adducts.<sup>29</sup> Recently, Yang has reported isolation of photochemical adducts of anthracene and dienes.<sup>30</sup>

Naphthalene disappearance upon quenching by 1,3-cyclohexadiene indicates adducts are also formed between this pair. Yang has independently obtained the same result and determined the adduct structures.<sup>31</sup> The absence of a dependence of adduct formation on 1,3-cyclohexadiene concentration as shown in Table IV means that 1,3-cyclohexadiene does not quench the

(28) Interpolated from the results of A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4781 (1966).

(29) (a) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4723 (1967); (b) K. Kraft and G. Koltzenburg, International Conference on Photochemistry, München, Sept 6-9, 1967.

(30) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 1406 (1972).

(31) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 9228 (1972).

**Table IV.** Singlet Quenching Study of Naphthalene with 1,3-Cyclohexadiene<sup>a</sup>

1,3-Cyclohexadiene, <i>M</i>	Naphthalene, <i>M</i>	$\phi_{\text{-naph}}$
0.294	0.090	0.17
0.496	0.090	0.17
0.762	0.090	0.17
0.867	0.090	0.18
1.235	0.200	0.17
2.041	0.200	0.17
4.084	0.200	0.19
0.496	0.043	0.18
0.496	0.090	0.17
0.496	0.207	0.16

<sup>a</sup> Cyclohexane as solvent. Solutions were irradiated at 313 nm and room temperature.

exciplex. This can be attributed to either a low quenching constant or a very short exciplex lifetime.

The third observation is complicated by inconsistent results and corrections due to residual triplet reactions that must be made. The conclusion is, however, that **1** is converted to **4** with a quantum yield of 0.07 (adjusted to complete fluorescence quenching) as a result of singlet quenching. Evidence for this is threefold. Quantum yields for the production of **4** are significant even after proper corrections are made. Isoprene quenches only the portion of the formation of **4** that is calculated to be of triplet origin. Third, the small amount of the isomerization ( $\phi = 0.019$ ) observed in the presence of 2,5-dimethyl-2,4-hexadiene, an efficient singlet quencher ( $k_q = 3.96 \times 10^9$  l./mol sec),<sup>3</sup> is within the experimental error of the value ( $\phi = 0.011$ ) calculated on the basis of the relative amounts of singlet quenching. Cis-trans isomerization can occur by two mechanisms; a cis-trans isomerization about the trans double bond (process C), or by a 1,5-hydrogen shift (process B) as suggested by Bloomfield and McConaghy for the thermal isomerization.<sup>17</sup> The possibility that a hydrogen shift could occur as a result of singlet quenching has been investigated previously with *cis*-2-methyl-1,3-pentadiene.<sup>32</sup> Despite a low activation energy for the process ( $E_a = 32.8$  kcal/mol),<sup>33</sup> isomerization was not detected. Because of this observation, process C is the favored mechanism for the isomerization observed here.

The chemical consequences of singlet quenching by **2** are simpler. A small amount of adduct formation again occurs as indicated by the naphthalene disappearance ( $\phi = 0.004$ ), and ring opening to form 2,3-dimethyl-1,3-butadiene ( $\phi < 0.001$ ) is not observed.

In summary, adduct formation is apparently a common consequence of fluorescence quenching. Processes A and D, which require considerable geometric changes, do not occur, while process C occurs but with an efficiency of about 15% of the quadricyclene<sup>12</sup> and sulfoxide<sup>13</sup> isomerizations. We believe that the wide range of results in nonclassical singlet quenching systems can be accommodated by a mechanism in which exciplex formation involves weakening and perhaps cleavage of one or two quencher bonds. Upon internal conversion of the exciplex, the partial bonds between the quencher and naphthalene either strengthen and adducts form or weaken and disso-

ciation occurs. In circumspection, we observe that, with the exception of exciplexes involving sulfoxides, dissociation leads to quencher isomerization only when strained bonds are intimately involved in exciplex bonding. Exciplex formation between naphthalene and quadricyclene undoubtedly involves weakening of the two cross-link bonds of quadricyclene. Upon dissociation of the exciplex, the quadricyclene moiety finds it can reform bonds by two pathways to yield norbornadiene or quadricyclene. As it is highly energetic, it does not feel the large ground state enthalpy difference between norbornadiene and quadricyclene<sup>34</sup> and proceeds in both directions with equal probability ( $\phi = 0.52$ ).<sup>12</sup>

For dienes, the exciplex interaction probably involves the entire  $\pi$  system. Hence, the  $\pi$ -bond order is not reduced significantly and exciplex dissociation does not lead to isomerization.

The lack of planarity as indicated by models for *cis,trans*-1,3-cyclooctadiene coupled with considerable strain make this diene atypical. It is very likely that the exciplex interaction is highly localized in the trans double bond. This does significantly reduce the  $\pi$  bond order, and, upon exciplex dissociation, the rate of bond rotation is comparable to the rate of bond reformation. This leads to the observed isomerization.

For 1,2-dimethylcyclobutene, the quenching rate is comparable to that of other olefins,<sup>32</sup> an indication that the exciplex interaction is localized in the  $\pi$  bond of **2**. Upon dissociation of the exciplex, vibrational energy is dissipated before the molecule can utilize the energy to undergo a ring opening.

While it is still possible to explain the isomerizations in terms of vibrational energy transfer, it is necessary to add the limitation that isomerization must occur upon the first vibration following exciplex dissociation. As we do not believe that significant geometric changes occur during the formation of the exciplex, this restricts isomerization to cases where minimal structural changes are required. Because of the complexities of the vibrational relaxation mechanism, the predictive ability of this approach seems very limited. On the other hand, we believe that a careful analysis of the nature of bonding in the exciplex could lead to accurate predictions concerning the possibilities for resultant isomerization.

The fit of sulfoxide racemizations into this mechanism deserves a brief comment. Although, the quantum yields for racemization ( $\phi = 0.4$ )<sup>13</sup> indicate that the sulfoxides are not planar in the exciplex, they could be very close to planarity. This is a case where upon dissociation of the exciplex the first vibration can easily cause racemization.

### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer or a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Nmr spectra were run on a Varian A-60 spectrophotometer. Ultraviolet spectra were taken on a Cary 14 spectrometer. Mass spectral services were performed by the Midwest Research Institute, Kansas City, Mo. The analyses of products were carried out on a F&M Model 500 or a Varian Aerograph Model A-90-P gas chromatograph. A Hewlett and Packard Model 776 preparative gas chromatograph was used for purifica-

(32) G. S. Hammond and S. L. Murov, unpublished results.

(33) H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965).

(34) Enthalpy difference is 23.9 kcal/mol: R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

tion of chemicals. Melting points and boiling points are uncorrected.

**Materials.** *n*-Pentane and cyclohexane (Fisher Scientific Co., Spectrograde) were used without further purification. Naphthalene (Baker Analyzed Reagent) was zone refined. Michler's ketone and *p*-phenylbenzophenone (Eastman Organic Chemical Co.) were recrystallized from ethanol with mp 171–172 and 101–102°, respectively. Isoprene (Aldrich Chemical Co., puriss), 1,3-cyclohexadiene, 2,5-dimethyl-2,4-hexadiene (Aldrich Chemical Co.), and 2,3-dimethyl-1,3-butadiene (Chemical Samples Co.) were purified by distillation from lithium aluminum hydride prior to use. *cis,cis*-Cyclooctadiene (Chemical Samples Co.) was eluted through a 5-cm neutral alumina column and distilled. *cis,trans*-1,3-Cyclooctadiene was prepared by the benzophenone-photosensitized reaction of *cis,cis*-1,3-cyclooctadiene following the method of Liu.<sup>25</sup> The material was stored at –77° to prevent dimerization. Bicyclo[4.2.0]oct-7-ene was prepared by a photosensitized reaction of *cis,cis*-1,3-cyclooctadiene at the boiling point of cyclohexane following the method of Liu.<sup>25</sup> *cis*-Cyclooctene (Columbian Carbon Co.) was purified on a preparative gc with an 80 in. × 0.75 in. 20% of SE-30 on Chromosorb W (30–60 mesh) column. *trans*-Cyclooctene was synthesized from cyclooctylamine (Aldrich Chemical Co.) by the method of Cope<sup>35</sup> and purified under the same conditions as described for the *cis* isomer. 1,2-Dimethylcyclobutene was prepared following a modified version of Crowley's method.<sup>36</sup> A 1% solution of 2,3-dimethyl-1,3-butadiene (Chemical Samples Co) in pentane was irradiated under nitrogen by using a Hanovia 450-W mercury lamp with a Vycor filter. The reaction was monitored on a Varian A-90-P gas chromatograph with a 20 ft × 0.25 in. 20%  $\beta,\beta'$ -oxydipropionitrile on Chromosorb W column (column temperature at 25°). The reaction was stopped when the amount of starting material ceased to diminish. *n*-Pentane was distilled off on a 16 in. spinning band column. The concentrated solution was treated with maleic anhydride in ether to remove the unreacted diene. The solution was washed thoroughly with aqueous sodium bicarbonate solution and then water. After the solution was dried over anhydrous sodium sulfate, the fractions were collected by spinning band column distillation. The boiling point is 68–69°, and the glc analysis showed no more than 0.01% 2,4-dimethyl-1,3-butadiene remained.

(35) A. C. Cope and R. B. Bach, *Org. Syn.*, **49**, 39 (1969).

(36) K. J. Crowley, *Tetrahedron*, **1001** (1965).

**Fluorimetry.** Relative fluorescence intensities measurements were made on a Perkin-Elmer constant energy fluorimeter at least twice for each sample. The instrument was modified to accept liquid samples by rotating it 90° from its normal position. Sample solutions (3 ml) in 13-mm Pyrex tubes were degassed by three freeze-pump-thaw cycles to  $5 \times 10^{-4}$  mm.

**Quantum Yields.** Samples for irradiation were held in a modified version of Merry-Go-Around<sup>26,27</sup> with a 450-W mercury lamp as a light source. A filter solution containing 0.023% K<sub>2</sub>CrO<sub>4</sub> and 0.1% NaOH which was circulated through a quartz dipper well (path length 0.44 cm) and a Corning 7-54 filter were combined to isolate the 313-nm mercury line. Ferrioxalate actinometry was used for measuring light intensities.<sup>26,28</sup> All product analyses after irradiation were performed by gas chromatography.

**Adducts** were prepared by irradiating sample tubes containing 0.234 M naphthalene and 0.445 M *cis,trans*-1,3-cyclooctadiene for a period such that at least a 50% conversion occurred. The mixture was then purified by preparative tlc and glc (2 ft × 0.25 in. 20% SE-30 on Chromosorb W as column at 190°). Three fractions were collected by glc with retention time 10.9, 13.7, and 16.3 min, respectively. Nmr spectra (CCl<sub>4</sub>) for fraction 1 (*R*<sub>t</sub> = 10.9 min) showed a broad singlet at  $\tau$  3.2 (4 H), a multiplet around 3.4–4.2 (2 H), and multiplets at 4.5–5.4 (2 H), 6.3–6.9 (2 H), 7.5–9.0 (10 H); fraction 2 (*R*<sub>t</sub> = 13.7 min) showed a broad singlet at  $\tau$  3.12 (4 H), multiplets at 3.9 (1 H), 4.0–5.0 (2 H), 6.0–6.3 (1 H), 6.5–7.0 (2 H), 7.5–9.0 (10 H); fraction 3 (*R*<sub>t</sub> = 16.3 min) showed a broad singlet at  $\tau$  3.25 (4 w), and multiplets at 3.6–5.0 (4 H), 6.4–7.2 (2 H), 7.2–9.5 (22 H). The nmr for fraction 3 could indicate a 1:2 naphthalene-*N*-1 adduct, however, mass spectra showed peaks at *m/e* 236 (parent peak, 1:1 adduct), 128 (major peak, naphthalene), and 108 (1,3-cyclooctadiene) for all three fractions. The peak at *m/e* 344 (parent peak for 1:2 naphthalene-1 adduct) was searched for carefully without any success.

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## Formation and Study of the $\alpha$ Monoanion and $\alpha,\alpha'$ Dianion of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one<sup>1</sup>

George B. Trimitsis,<sup>\*2a</sup> Ernest W. Crowe,<sup>2a</sup> George Slomp,<sup>2b</sup> and Todd L. Helle<sup>2a</sup>

Contribution from the Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001, and Research Laboratories, The Upjohn Company, Kalamazoo, Michigan 49001. Received December 18, 1972

**Abstract:** 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) has been converted to its monoanion **8** and its dianion **9**. It was found that the negative charge in dianion **9** was delocalized not only into the carbonyl group and the two phenyl rings, but also into the carbon-carbon double bond at C<sub>6,7</sub>, thereby making the 2,4-diphenylbicyclooctenone dianion **9** the first homoaromatic analog of the six  $\pi$ -electron aromatic cyclopentenone dianion **6**. Monoanion **8** was found to exist as a mixture of two isomeric enolates **8a** and **8b** in a ratio of 2:1, respectively. This ratio was shown to be solvent independent. It was further established that there was no interaction between the negative charge at C<sub>2</sub> and the C<sub>6,7</sub> olefinic group in either isomer. Rationalizations are offered for these observations, and the properties of the 2,4-diphenylbicyclooctenone enolate monoanions **8a,b** are compared and contrasted with those of the enolates derived from simple 2,6-disubstituted cyclohexanones.

The stabilization of carbanions and carbonium ions by means of cyclic charge delocalization or aromaticity is well documented<sup>3</sup> and universally accepted.

(1) Taken largely from the M. A. dissertation of E. W. Crowe, Western Michigan University, 1972.

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