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VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1 H-
AZEPINE AND ITS THERMAL REVERSION. QUANTITATIVE ASPECTS

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VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE
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Guilford Jones, II* and Laura J. Turbini
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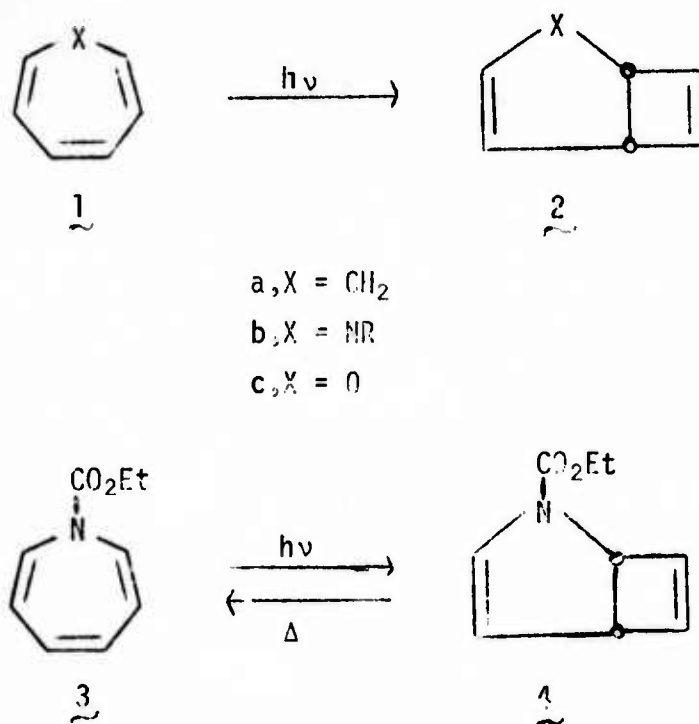
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ABSTRACT

Photolysis of 1-ethoxycarbonyl-1H-azepine (3) at 325 - 385 nm gives quantitatively the valence isomer, 2-ethoxycarbonyl-2-azabicyclo(3.2.0)hepta-3,6-diene (4). The quantum yield in benzene is 0.013 and is virtually unchanged in other solvents including n-propyl bromide and with the addition of triplet quenchers. Sensitization with fluorenone, benzophenone, or valerophenone does not affect valence isomerization. Azepine 3 acts as a quencher of the photoelimination of valerophenone ( $k_q = 7.0 \times 10^9 \text{ l}^{-1} \text{ sec}^{-1}$ ) and the phosphorescence of biacetyl ( $k_q = 5.3 \times 10^8 \text{ l}^{-1} \text{ sec}^{-1}$ ). Laser photolysis at 457.9 nm affects isomerization 3  $\rightarrow$  4 with a quantum efficiency of 0.013. On the basis of absorption, sensitization, and quenching data for 3, energies of low lying excited states are estimated ( $E_{S_1} = 60 \pm 1 \text{ kcal/mol}$  and  $E_{T_1} = 55 \pm 1 \text{ kcal/mol}$ ). Pyrolysis of 4 gives 3 in a clean, exothermic, first order reaction at 113 - 143° in diglyme- $d_{14}$  ( $E_a = 28.7 \text{ kcal/mol}$ ,  $A = 10^{12.3} \text{ sec}^{-1}$ ) or in hexadecane ( $k = 4.60 \times 10^{-4} \text{ sec}^{-1}$ , 127.5°). The mechanism suggested for photochemical isomerization 3  $\rightarrow$  4 and its thermal reversion involves a common diradical-zwitterionic intermediate. Emphasis is placed on the importance of charge separation in such an intermediate, the geometry of which facilitates radiationless decay from the excited surface to bicyclic product. Isomerization 3  $\rightarrow$  4 may be "cycled" in sequential photochemical and thermal steps with good chemical efficiency, providing a model for the storage and conversion of photochemical energy.

The photochemistry of 1,3,5,-cycloheptatriene (1a), its heterocyclic analogs, 1H-azepine (1b) and oxepin (1c), and their derivatives has received considerable attention.<sup>1</sup> A reaction of general importance is valence photoisomerization to bicyclic dienes 2; in many cases the process is thermally reversible. We became interested in the photoisomerization of 1-ethoxycarbonyl-1H-azepine (3), since the reported<sup>1d</sup> behavior of this system showed promise for the storage and conversion of (in principle, a portion of solar energy) electronic energy. In particular, photolysis of 3, which absorbs light in the visible, gives 4 cleanly and photochromically (with bleaching). Photoisomer 4 is kinetically stable but reverts to 3 in a thermal reaction which is uncatalyzed and apparently exothermic.<sup>1d</sup> We wish to provide quantitative details concerning this isomerization of a sort not generally available for the cyclic trienes, which allow identification of states and suggestions for pathways for photochemical and thermal reaction. The discussion will bear on the relationship between ground and excited state potential surfaces for such systems.



## Results

The ultraviolet spectrum of  $3^2$  displays a weak transition at 330 nm. This absorption, which is blue shifted in polar solvent and probably  $n, \pi^*$  in character,<sup>3</sup> tails into the visible with onset at ~~about 430 nm~~ and gives  $3$  its orange color. Luminescence was not observed for  $3$ , either in benzene at room temperature or in EPA glass at 77°K. Irradiation of  $3$  at 325-385 nm gave  $4$  without the appearance of side products (> 97% yield by glc and nmr). Quantum yields for isomerization as a function of solvent and the presence of additives are shown in Table I. Notably, the photolysis was not appreciably altered by (1) moderate concentrations of potential quenchers of excited triplets, 2,5-dimethyl-2,4-hexadiene and cyclooctatetraene, (2) a heavy atom<sup>5</sup> reagent, *n*-propyl bromide, as solvent, or (3) the addition of dimethylacetylenedicarboxylate (DIAC), a good dipolarophile.<sup>6</sup>

In experiments where photosensitizers, benzophenone ( $E_T = 69$  kcal/mol), fluorenone ( $E_T = 53$  kcal/mol) and valerophenone, absorbed most of the light, photoisomerization of  $3$  was negligible. That the excited triplet of  $3$  could in fact be produced was inferred from experiments in which the photoelimination of valerophenone to acetophenone<sup>7</sup> was quenched. Measurement of  $\phi_0/\phi$  at two concentrations of  $3$ , 4.5 and  $6.6 \times 10^{-3}$  M, gave  $k_q \tau = 56 \pm 8$  M<sup>-1</sup>, from which the quenching constant,  $k_q = 7.0 \times 10^9$  M<sup>-1</sup> sec<sup>-1</sup>, could be calculated assuming  $\tau$  (valerophenone) =  $8.0 \times 10^{-9}$  M<sup>-1</sup> sec.<sup>8</sup> For comparison the estimated rate constant for diffusion controlled quenching, according to the modified Debye equation,<sup>9</sup> in benzene at 30° is  $1.8 \times 10^{10}$  M<sup>-1</sup> sec<sup>-1</sup>, and the "upper limit" quenching constant for dienes in benzene (25°) has been determined in several studies to be  $5 \times 10^9$  M<sup>-1</sup> sec<sup>-1</sup>.<sup>9</sup> Quenching of the phosphorescence of biacetyl with  $1.0 - 4.0 \times 10^{-5}$  M azepine was observed at room temperature. From the plot of  $\phi_0/\phi$  vs.  $[3]$ ,  $k_q \tau = 2.5 \pm 0.3 \times 10^5$  M<sup>-1</sup> was obtained, from which  $k_q = 5.3 \times 10^8$  M<sup>-1</sup> sec<sup>-1</sup> could be calculated assuming  $\tau$  (biacetyl) =  $4.6 \times 10^{-4}$  sec.<sup>10</sup>

Table 1. Quantum Yields for Photoisomerization  $3 \rightarrow 4$ .

| [3]   | Solvent              | Additives (II)                   | $\eta^a$            |
|-------|----------------------|----------------------------------|---------------------|
| 0.08  | cyclohexane          | ----                             | 0.010               |
| 0.09  | diglyme <sup>b</sup> | ----                             | 0.013               |
| 0.10  | Benzene              | ----                             | 0.013               |
| 0.03  | n-propyl bromide     | ----                             | 0.013               |
| 0.08  | benzene              | COT <sup>c</sup> (0.11)          | 0.014               |
| 0.10  | benzene              | diene <sup>d</sup> (0.02 - 0.08) | 0.012               |
| 0.10  | benzene              | fluorenone <sup>e</sup> (0.9)    | <0.003 <sup>g</sup> |
| 0.09  | benzene              | benzophenone <sup>f</sup> (1.0)  | <0.003 <sup>g</sup> |
| 0.007 | benzene              | valerophenone <sup>f</sup> (0.4) | <0.003 <sup>g</sup> |
| 0.03  | benzene              | D1AC <sup>h</sup> (0.03)         | 0.010 <sup>i</sup>  |

<sup>a</sup>Rayonet reaction (355  $\pm$  30 nm), 30  $\pm$  1°C, valerophenone actinometer (ref 4), estimated error,  $\pm$  15%. <sup>b</sup>bis(2-methoxyethyl) ether. <sup>c</sup>Cyclooctatetraene. <sup>d</sup>2,4-dimethyl-2,5-hexadiene. <sup>e</sup>Sensitizer absorbed 88% of light. <sup>f</sup>Sensitizer absorbed 75% of light. <sup>g</sup>Upper limit corrected for azepine absorption. <sup>h</sup>Dimethyl acetylenedicarboxylate. <sup>i</sup>Some light absorption by D1AC.

Sealed ampoule pyrolysis of  $4$  proceeded nearly quantitatively in solvents at temperatures above 100°. Appearance of  $3$  (nmr analysis) was smoothly first order over two half-lives. The results are shown in Table 2 along with activation parameters for pyrolysis in diglyme- $d_{14}$ . The kinetics are in good agreement with the approximate rate data for pyrolysis of neat  $4$ , reported by Paquette and Barrett<sup>1d</sup> from which  $k(4 \rightarrow 3, 126.5^\circ) = 6.6 \times 10^{-4} \text{ sec}^{-1}$  may be calculated.



Table 2. Kinetics of the Thermally Induced Isomerization 4 → 3

| Solvent                 | Temperature (°C) | k (10 <sup>4</sup> sec <sup>-1</sup> ) | E <sub>a</sub> = 28.7 kcal/mol<br>A = 10 <sup>12.3</sup> sec <sup>-1</sup> |
|-------------------------|------------------|----------------------------------------|----------------------------------------------------------------------------|
| diglyme-d <sub>14</sub> | 112.5            | 1.45 ± 0.06                            |                                                                            |
|                         | 122.5            | 3.44 ± 0.15                            |                                                                            |
|                         | 127.5            | 5.34 ± 0.05                            |                                                                            |
|                         | 133.0            | 8.21 ± 0.58                            |                                                                            |
|                         | 142.5            | 19.3 ± 0.11                            |                                                                            |
| hexadecane              | 127.5            | 4.60 ± 0.44                            |                                                                            |

The photoisomerization 3 → 4 could be affected in direct sunlight and with use of an argon ion laser. The quantum yield for isomerization at 457.9 nm in benzene was 0.013. The valence isomers could be "cycled". A sealed Pyrex tube containing 3 and 4 in diglyme-d<sub>14</sub> was alternately irradiated (sunlight or near UV) and pyrolyzed (generally 130°). The isomerizations were followed to high conversion by nmr (benzene internal standard). Although the photochemical step was extraordinarily clean, the back reaction built up a small amount of byproduct (dimer<sup>11</sup> or polymer), such that after ten passes material balance was about 50%.



## Discussion

The failure of dienes, 2,4-dimethyl-2,5-hexadiene ( $E_T < 53$  kcal/mol<sup>12</sup>), a well known efficient quencher of reasonably long lived excited triplets,<sup>9</sup> and COT, for which a very low triplet energy has been calculated,<sup>13</sup> to alter the photolysis of 3 implicates a reactive singlet state for valence isomerization. The sensitization data, in which common energy transfer agents representing a range of triplet excitation energies ( $E_T$  53 - 73 kcal/mol<sup>14</sup>) are ineffective, confirm that a singlet state (probably of  $n, \pi^*$  character) is responsible for formation of 4. The quenching of valerophenone photoelimination at a rate near the diffusion limit further establishes that a triplet state of 3 is accessible but unreactive. That datum and the inefficiency with which 3 quenches the phosphorescence of biacetyl ( $E_T = 55 - 56$  kcal/mol<sup>16</sup>) bracket the energy of the lowest triplet of azepine at  $\sim 55$  kcal/mol.<sup>17</sup>

The  $n, \pi^*$  absorption for 3 ( $\lambda_{\max}$  330 nm, tailing past 450 nm) and the success of laser photolysis at 458 nm (61 kcal/Einstein), a wavelength which must be very close to the 0-0 transition, narrow the acceptable range for the energy of  $S_1$ . Values of  $E_{S_1} = 60 \pm 1$  and  $E_{T_1} = 55 \pm 1$  kcal/mol would be consistent with the data and allow for a reasonable  $n, \pi^*$  singlet-triplet separation. This placement of singlet and triplet levels may be of general use for the heterocyclic triene systems in the absence of luminescence data.

Interestingly, the existence of a very low lying triplet (e.g.,  $E_T < 50$  kcal/mol), analogous to "aromatic" species ( $\pi, \pi^*$  triplets) predicted for cyclic polyenes having formally 4n cyclic electronic arrays which enjoy resonance stabilization,<sup>13</sup> or analogous to triplet 1a ( $E_T = 47$  kcal/mol<sup>1c</sup>) appears unlikely for 3. On the other hand, it is improbable that the  $\pi, \pi^*$  triplet would lie much above 60 kcal/mol if 3 be diene-like.<sup>11</sup> Further speculation is (1) that the  $n, \pi^*$  and  $\pi, \pi^*$  triplet levels are closely spaced (slightly below the  $S_1$   $n, \pi^*$  level) (2) that intersystem crossing to the higher lying  $\pi, \pi^*$  state is facile<sup>18</sup> and accounts at least in part for the low efficiency of valence isomerization and (3)

that the effect of heavy atom solvent on the quantum yield is minimal since depletion of  $S_1$  through intersystem crossing is intrinsically rapid.<sup>19</sup>

Data for 3 completes an excited state structure - reactivity pattern (Table 3) for several cyclic polyene systems which have been the object of comparison in numerous studies.<sup>20</sup> Excited singlets in the series are uniformly reactive (albeit inefficiently where measured), whereas triplets do not bring about valence isomerization.<sup>24</sup> The latter is noteworthy in view of the established reactivity under sensitization conditions of diverse seven and eight membered conjugated cyclic dienes and trienes such as 1,3-cyclooctadiene,<sup>25</sup> cyclohepta-3,5-dien-1-one,<sup>26</sup> a derivative of 2-aza-1,3-cycloheptadiene,<sup>27</sup> and including cycloocta-2,4,6-trien-1-one<sup>23</sup> (where the reactive state is most likely a triplet for direct irradiation). A mechanism considered for valence isomerization in each case involves cis-trans isomerization via the excited triplet to a strained ring system (with formally one trans double bond), which ring-closes to bicyclic product in a symmetry unrestricted thermal reaction. Such a course for trienes 1 is shown below in which 5 is one of several possible geometric photoisomers of 1. In two of the previous studies,<sup>25,23</sup> the intermediate analogous to 5 has been either isolated or trapped. The failure of triplets of 1 to give bicyclic product probably reflects the relatively more

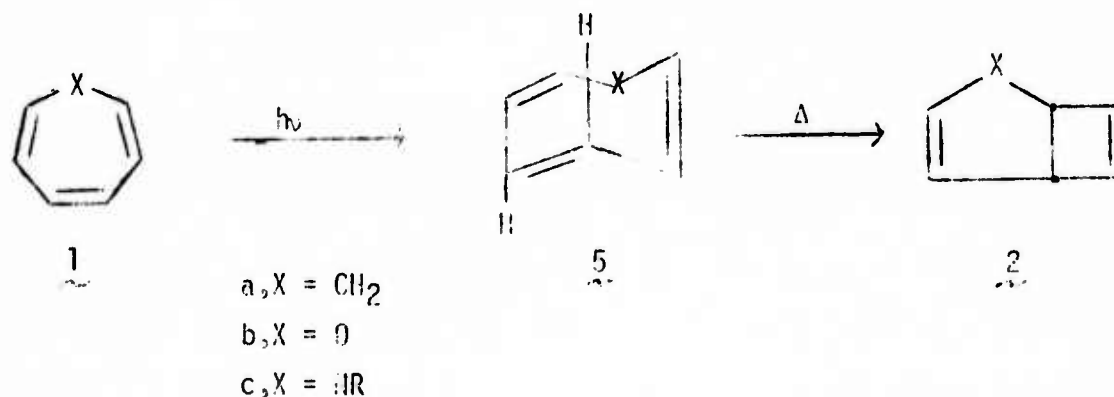


Table 3. Photolysis and Pyrolysis Characteristics for Selected Reversible Valence Isomerizations.<sup>a</sup>

| Cyclic<br>Polyene | $\xrightleftharpoons[\Delta]{h\nu}$ | Bicyclic<br>Diene | Direct<br>Irradiation   | Sensitized<br>Irradiation | Ref          | E <sub>a</sub> , kcal/mol <sup>d</sup> | (ref)        |
|-------------------|-------------------------------------|-------------------|-------------------------|---------------------------|--------------|----------------------------------------|--------------|
| 1a                |                                     | 2a                | X<br>( $\phi = 0.010$ ) | 0                         | 1a,c         | 39.5                                   | (21)         |
| 1c                |                                     | 2c                | X                       | 0                         | 1h           | ---                                    |              |
| 3                 |                                     | 4                 | X<br>( $\phi = 0.013$ ) | 0                         | This<br>work | 20.7                                   | This<br>work |
| COT <sup>b</sup>  |                                     | BOT <sup>c</sup>  | X                       | 0                         | 22           | 13.7                                   | (23)         |

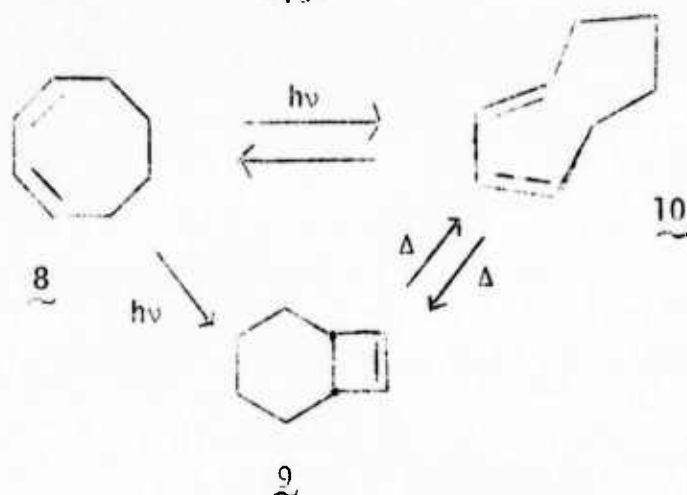
<sup>a</sup> X = isomerization of polyene observed; 0 = isomerization of polyene unobserved.

<sup>b</sup> 1,3,5,7-cyclooctatetraene. <sup>c</sup> Bicyclo(4.2.0)octa-2,4,7-triene. <sup>d</sup> Activation parameters for thermal back reaction; log A values for 2a, 4, and BOT are 14, 12.3, and 12.0, respectively.

severe restrictions due to bond angle strain in 5 compared to the other twisted cyclopolyenes (molecular models show this impressively). Triplet COT may indeed reach a configuration analogous to 5 but the overall result is formation of semi-bullvalene.<sup>22c</sup>

Excited singlets of 1 may give intermediates 5 prior to valence isomerization. Indeed there is direct evidence that 1,3,5-cyclooctatriene (6)<sup>29</sup>, 1,2,4,7-tetraphenylcyclooctatetraene (7)<sup>30</sup> and 1,3-cyclooctadiene (8)<sup>31</sup> give geometric isomers on direct irradiation. The isomers of 6 and 8 may lead to valence isomeric bicyclic polyenes, while the isomer of 7 may be responsible for formation of diphenylacetylene and p-terphenyl (via a bicyclic triene).<sup>30b</sup> However, Hebe and Fonken have shown that 8 gives 9 under conditions where geometric isomer 10 is stable. In addition, thermal reversion to 7, from its geometric photoisomer is "quantitative",<sup>30a</sup> meaning that valence photoisomerization of 7 by way of a geometric isomer is extremely inefficient if not absent.

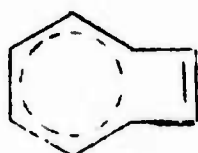
The point here is that in the singlet manifold for the cyclic dienes and trienes, there exists a path for ring closure to a bicyclic isomer which does not require formation of a geometric isomer. For the cyclic polyene triplets valence isomerization proceeds through prior cis-trans isomerization and thermal ring closure, but <sup>only</sup> where the geometric isomer is accessible on geometric grounds (not the case for trienes 1) and reactive enough to give bicyclic product under photolysis conditions (marginally the case for 8<sup>31</sup>).<sup>32</sup> After examination of the thermal surface for 4 → 3, we will return to the mechanism of singlet valence isomerization of 3.



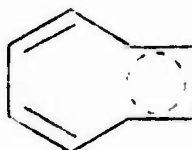
Circumstantial arguments may be brought against two mechanisms for the thermal isomerization  $4 \rightarrow 3$ . The first mechanism involves formation of 5 via conrotatory ring opening of 4, following the suggestion of Baldwin and Kaplan<sup>33</sup> in their study of ring openings of bicyclic dienes. Such a mechanism is apparent in the thermal degenerate rearrangement which accompanies valence isomerization of deuterium labeled bicyclo(4.2.0)octa-2,7-diene<sup>34</sup> and in the pyrolytic ring opening of 9.<sup>35</sup> The evidence for the appearance of cis-trans isomers comes again for the more flexible ring systems, in fact those cases where the strained geometric isomers are available photochemically from the all-cis cyclic polyenes.<sup>25,29,31</sup> The acceleration of pyrolysis for 4 compared to 1a does not support a general mechanism involving a cis,trans,cis intermediate. Aside from the geometric difficulties in 5, it is difficult to see how the energy barrier for ring opening of 4 (an overall rate determining, symmetry unrestricted step which would respond more likely to steric and bond angle strain effects than to electronic effects) could be reduced by 11 kcal/mol by substituting -NR- for -CH<sub>2</sub>-.

Thermal disrotatory ring opening of 4 may give 3 directly in a concerted process. It is apparent from the magnitude of the activation energy for valence isomerization (Table 3) that BOT enjoys significant six-electron transition state stabilization (11) (for disrotatory opening, a 6e Huckel<sup>36</sup> aromatic<sup>37</sup> system) and suffers

little from four-electron destabilization such as in 12 (a 4e Hückel, antiaromatic transition state).<sup>38</sup> Ring opening of 4 could likewise benefit from the importance of 13, to the extent that the lone pair on nitrogen could contribute to a pyrrole-like aromatic sextet.<sup>39</sup>



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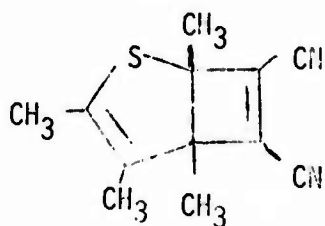


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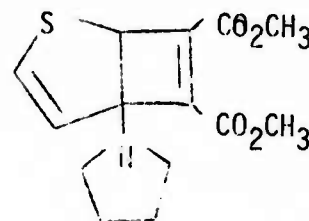


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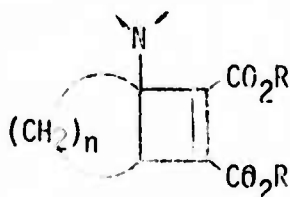
However, the heteroatom substituent effect appears to be more general and manifest in accelerations of thermal disrotatory ring openings of fused cyclobutenes in which a stabilizing six electron transition state cyclic array is not available. For example 14 is thermally stable, while 15 ring opens readily.<sup>40</sup> Likewise cycloadducts 16 of dimethyl acetylenedicarboxylate and cyclic enamines are generally unstable even near room temperature with respect to ring opening to 17.<sup>41</sup>



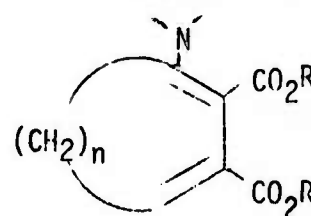
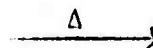
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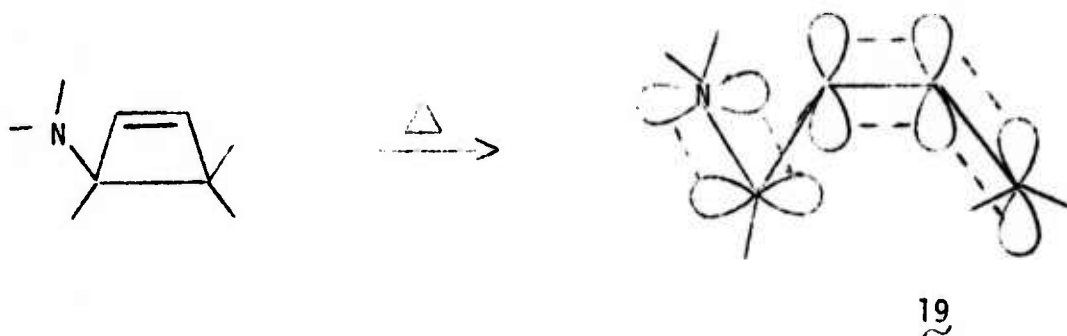
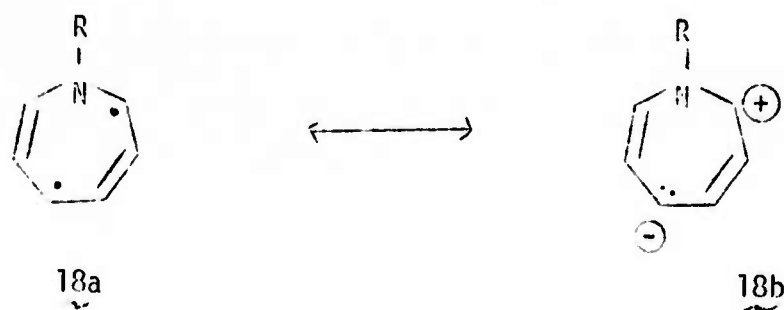


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We prefer a mechanism for the thermal isomerization  $4 \rightarrow 3$  involving a non-synchronous ring opening in which all-cis  $3$  emerges following motions which are overall dirotatory but where pi bond development in  $3$  lags bond breaking in  $4$  early along the reaction coordinate. In the extreme a two step path including di-radical intermediate  $18$  (geometry unspecified) would be important. Orbital overlap for such a species (from  $4$ ,  $15$ , or  $16$ ) as in  $19$  might be important. O'Neal and Benson<sup>42</sup> have suggested a diradical path for ring opening of bicyclo(3.2.0)hept-6-ene (a fused cyclobutene similar to  $4$ ), and the activation parameters for the isomerization  $2a \rightarrow 1a$  have been considered not inconsistent with the diradical formulation.<sup>21</sup> Our analysis respects the basic similarity between isomerizations  $2 \rightarrow 1$  and the disrotatory cyclobutene  $\rightarrow$  1,3-butadiene ring opening, an interconversion of "lumomers,"<sup>43</sup> for which an orbital crossing and a diradical intermediate are predicted with support from semi-empirical calculation of the isomerization potential surface.<sup>44</sup>





Diradical 18 may well have more complicated electronics than that associated with canonical form 18a (product of homolytic ring opening). The transition state for formation of the latter would be stabilized relative to that for 2a by an amount associated with the degree to which the carboxamido group ( $\text{RCONH}^-$ ) stabilizes a radical center. This value is unknown but may be approximated by the effect of the acyloxy ( $\text{RCO}_2^-$ ) substituent on C-H bond dissociation energies ( $\Delta\text{BDE} < 1 \text{ kcal/mol}$ ).<sup>45</sup> The reduction in activation energy for 4 vs. 2a (11 kcal/mol) is inconsistent with this kind of transition state stabilization. An alternative view recognizes the extent to which the odd electron centers in 18 interact with adjacent polarizing fragments (e.g., 19). Respecting the electron releasing ability of nitrogen, contributing structures of the type 18b gain importance and in molecular orbital terms the singlet diradical wave function has considerable ionic character.<sup>46</sup> In the extreme, intermediate 18 would be a discrete zwitterion as suggested by Criegee and coworkers<sup>47</sup> for ring opening of highly polarized cyclobutenes. Epiotis has also pointed out the importance of polarizing substituents on the rates of electrocyclic reactions.<sup>48,49</sup>

Quantitative estimation of transition state stabilization due to charge separation (i.e., the importance of 18b) for pyrolytic cyclobutene ring openings is difficult. It would depend of course on substituent polarizing ability and interaction with solvent. A solvent effect on the rate of pyrolysis of 4 (Table 2) is absent; however, in several studies in which 1,3 or 1,4 dipoles have been implicated, modest solvent dependence has been observed.<sup>50</sup> On the other hand, the substituent effect on the rate of ring opening of 15 and 16 appears to be quite large,<sup>51</sup> whereas substituent influence in 4 is predictably<sup>39</sup> intermediate.

The formulation of an intermediate (a secondary minimum) for the ground state surface 4  $\rightarrow$  3 is important in terms of current theories concerning modes of reactive

radiationless decay of excited species. We propose an energy surface relationship as shown in the Figure , which is consistent with photochemical and thermal data and includes all experimental quantities which are readily accessible. (The heat of reaction  $4 \rightarrow 3$  has been measured by differential scanning calorimetry.<sup>52</sup>)

The scheme submits to the following considerations. (1) Isomerization  $3 \rightarrow 4$  is a G-type photochemical reaction<sup>53</sup> in which adiabatic formation of the excited state of product is energetically prohibited<sup>54</sup> and dissociation into fragments is not important. (2) The aforementioned similarity with cyclobutene ring opening requires that the ground state isomerization  $4 \rightarrow 3$  be "forbidden" involving at some point along the reaction coordinate a formal HOMO-LUMO orbital crossing.<sup>43</sup> (3) The orbital crossing or avoided crossing<sup>55</sup> provides an orbitally degenerate (diradical) ground state in proximity with a minimum or "funnel"<sup>56</sup> in the excited singlet manifold, radiationless transition between which is facilitated. (4) The minimum in the triplet surface will occur at a loose geometry (flexible somewhat flattened ring) resembling more the boat-like ground state of 3, whereas the minimum or funnel in the singlet surface will assume a tight geometry (more folded or "pinched", less flexible ring, the geometry of diradical 18) resembling more the ground state of 4.<sup>56</sup>

Decay from  $S_1$  proceeds with little or no activation (no accompanying fluorescence) by way of mixing with an upper doubly excited singlet, the actual state of intended crossing with the ground configuration.<sup>57</sup> The inefficiency of valence isomerization may be understood in terms of competing intersystem crossing to  $T_1$  (vide supra, provided that  $S_1$  reach some minimum which would allow time for spin flipping) or in terms of uneven partitioning of an intermediate (19) (favoring 3 over 4), as expected in view of the skewed nature of the energy storing ground surface.<sup>58</sup>

Consideration of ionic character for 18 provides an explanation for the accelerated rate of pyrolysis of 4 and other polarized cyclobutenes confined to dis-

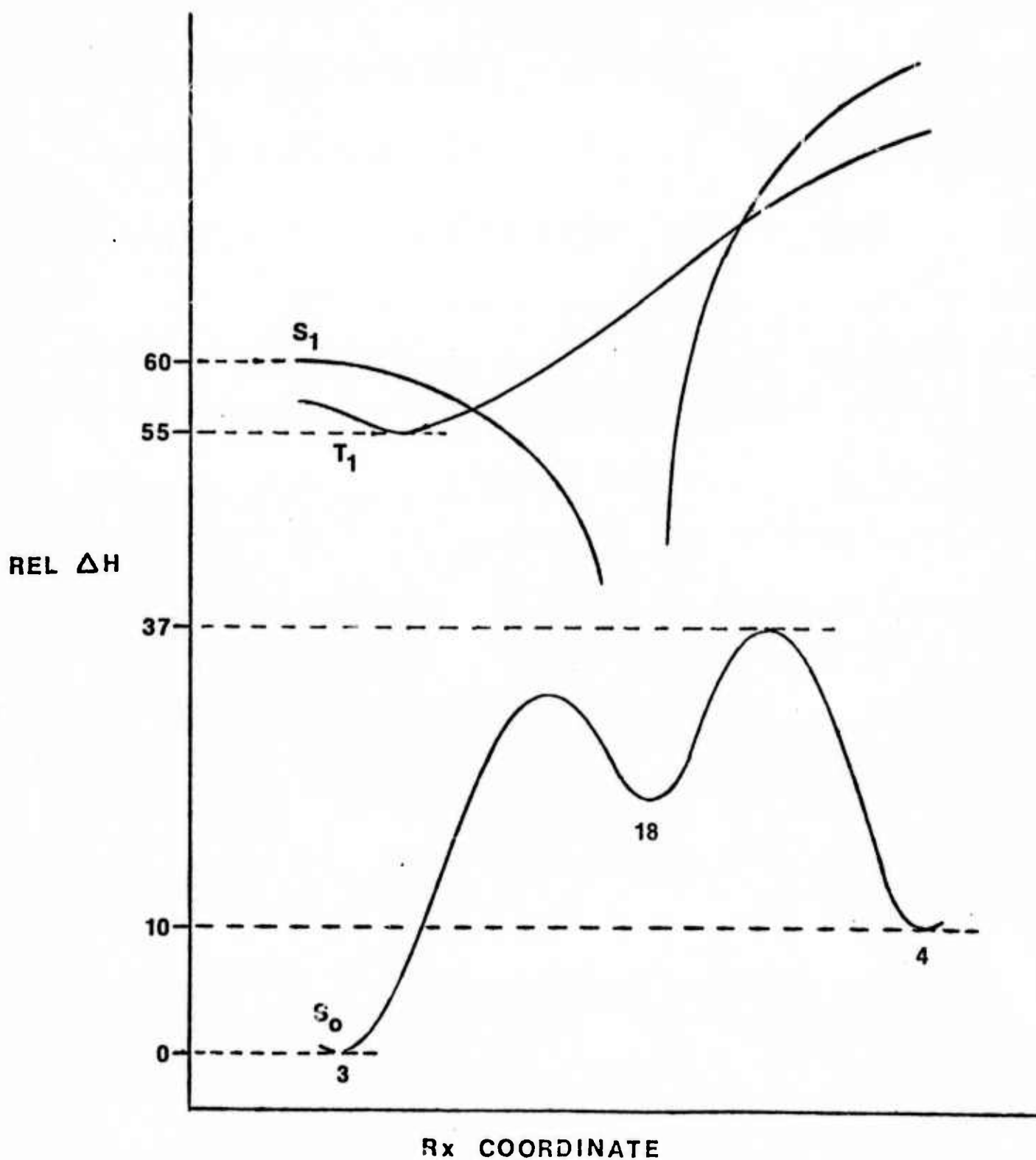


Figure. Potential energy surfaces for the photochemical and thermal interconversions of 3 and 4.  
 $\Delta H^\ddagger(4 \rightarrow 3, 128^\circ) = 27 \text{ kcal/mol.}$

rotatory ring opening. Development of charge appears to be important for photochemical ring closure as well. Electron releasing substituents are known to enhance valence isomerization of cycloheptatrienes<sup>59</sup> and tropones.<sup>60</sup> This structure-reactivity pattern implicates generally a ground-excited energy surface relationship in which the excited surface is increasingly directed (funnelled) to a tighter geometry at which radiationless transition occurs (making valence isomerization more favorable) as the diradical ground state becomes more ionic.<sup>56,61</sup> The excited triplet is correspondingly ineffective in bringing about valence isomerization because its minimum will occur at a loose geometry inappropriate for ring closure to bicyclic product.

The depth of the potential well for 18 will depend on solvent and substituent stabilization of charge and is of unknown size.<sup>62</sup> Efforts to trap such a species generated photochemically with a good dipolarophile, DNAC, were not successful. This places a short but uncertain lifetime on 18; if the quantum efficiency for 3 depends solely on partitioning of 18, a barrier of about 3 kcal/mol would be required leading to 4.<sup>58</sup>

In summary, the reactive state for photochemical valence isomerization 3 → 4 has been identified as an  $n, \pi^*$  singlet with a  $S_0 - S_1$  energy separation of about 60 kcal/mol. The lowest triplet of 3 is unreactive and has an energy above ground state of about 55 kcal/mol. Mechanisms for photolysis 3 → 4 and pyrolysis 4 → 3 are complimentary, in that the "forbidden" nature of the thermal reaction provides a region of surface into which the excited singlet funnels or near which there is an excited state minimum for facile radiationless decay. This region of surface near the formal crossing for ground and excited configurations is best formulated as a diradical-zwitterion (18). Partial charge developed and stabilized in such a species is important not only in lowering the barrier for pyrolysis (4 → 3) but

also in providing a tight geometry, facilitating photochemical ring closure to <sup>energy-rich</sup> ~~bi-~~ cyclic product (3 → 4). The results and suggested mechanism have implications for the isomerization of cyclic trienes (1 → 2) generally and provide another look at a thermally reversible <sup>endoergic</sup> photochemical process. Systems of this sort, for which extensive experimental detail is available, are still rare. They supply uniquely information for the evaluation of surface relationships which is of current theoretical interest, and in a practical vein they provide prototypes for the photochemical storage and conversion of radiated (solar) energy.

### Experimental Section

General. 1-Ethoxycarbonyl-1H-azepine (3)<sup>2</sup> was photolyzed in acetonitrile on a preparative scale (Hanovia immersion apparatus) to give 4 following generally the procedure of Paquette and Barrett.<sup>1d</sup>

Benzene, cyclohexane and n-propyl bromide were purified for use in photolysis by washing with 1) sulfuric acid 2) aqueous NaHCO<sub>3</sub> and 3) distilled water followed by distillation from P<sub>2</sub>O<sub>5</sub> or sodium. Valerophenone (Aldrich) was distilled under reduced pressure. Biacetyl was purified by spinning band distillation (bp 87-88°). Diglyme was distilled over sodium. Cyclooctatetraene, 2,4-dimethyl-2,5-hexadiene, fluorenone, and dimethyl acetylenedicarboxylate were commercial reagent grade materials used as received.

Varian 920 (tc detector) and 1400 (fi detector) instruments were used for analytical glc. Columns employed were (A) 5 ft x 1/4 in, 3% SE 30 on 100/120 Varaport-30 and (B) 8 ft x 1/8 in, 3% FFAP on Chrom-W.

Quantum Yields. Solution samples in 15 mm stoppered cylindrical Pyrex tubes were

irradiated in a Rayonet chamber reactor (Model RPR 204) equipped with RUL 3500A lamps and a merry-go-round accessory (Model HGR 100) (Southern New England Ultraviolet Co.). Samples were purged with nitrogen prior to irradiation. Solutions of 3 in the appropriate solvents (with additives) were irradiated in parallel with valerophenone (0.4 M in benzene) which served as actinometer and for which a quantum yield of production of acetophenone of  $0.33^A$  was assumed. Concentrations for all parallel irradiation samples were employed which insured complete absorption (measured absorbance  $> 1$  at 0.1 path maximum) over the range of lamp emission (325-385 nm). Samples were analyzed by glc for the appearance of 4 (column A, 100°, vs. 3) and acetophenone (column B, 150°, vs. dodecane internal standard). Quantum yields are averages of at least two runs at low conversions of valerophenone (~15%) and 3 (5-10%). Statistical analysis of area ratios for 4 (area from cut out and weigh procedure) and acetophenone (area from disc integration) in replicate runs indicated a precision of  $\pm 15\%$ .

Quenching of Valerophenone Photoelimination. The appearance of acetophenone from valerophenone was monitored as previously indicated for samples of valerophenone in benzene with increasing concentrations of 3. Relative amounts of acetophenone formed, obtained with good precision ( $\pm 5\%$ ), were used for  $\phi_0/\phi$ . Values were corrected for competitive absorption by 3 by computing relative absorbances at several wavelengths in the region of lamp emission. This correction became significant at higher concentrations of 3, and at lower concentrations, values of  $\phi_0/\phi$  were within experimental error of 1.0; therefore, quenching behavior was assessed only over a limited range.

Luminescence Experiments and Biacetyl Phosphorescence Quenching. Using an Hitachi Model MPF fluorescence spectrophotometer, emission from 3 was undetectable for samples at room temperature (0.02 M in benzene) and at 77°K (EPA glass, 0.001M).



The phosphorescence emission of biacetyl in benzene ( $\lambda_{\text{max}}$  522 nm) at room temperature was monitored as a function of 3. Samples were degassed through several freeze-thaw cycles on a vacuum line. Relative intensities at the emission maximum gave  $I_0/I$ . The fluorescence of biacetyl was not quenched with the addition of 3.

Pyrolysis Experiments. Samples of 4 in diglyme- $d_{14}$  or hexadecane (with benzene internal standard) were degassed in cleaned medium wall Pyrex nmr tubes (Hilmad Co.). Sealed ampoules were pyrolyzed in an insulated oil bath, thermostated using a Thermo-watch (Instruments for Research and Industry) and a calibrated ASTM thermometer. Temperature fluctuation was  $< 0.5^\circ$ . Ampoules were quenched and analyzed by nmr. Formation of 3 was followed by the appearance of a multiplet at 5.58 (vinyl C - H) and disappearance of 4 was monitored with reference to signals at 4.9 and 5.2  $\delta$  (multiplets,  $C_1$  and  $C_4^{1d}$ ). In experiments where benzene signal integration was used as an internal standard, a material balance for isomerization of  $> 95\%$  was obtained. Rate constants were calculated from the integrated first order rate equation and errors are average deviations for at least four points at each temperature.

Laser Photolysis of 3. Samples of 3, 0.1 M in benzene, were irradiated with an argon ion laser (Spectra-Physics, Model 164). The emission at 457.9 nm (rated at 250 mW) was focused on the optically flat circular window of a standard 5 cm Pyrex cell containing sample. Beam intensity was checked by irradiation of a 10 cm cell containing potassium ferrioxalate <sup>64</sup> actinometer solution. The quantum yield for appearance of Fe(II) was assumed to be 0.95. Concentrations of sample and actinometer solutions were employed which insured complete absorption of incident light. With a beam intensity of  $1.05 \pm 0.05$  mE/hr, a measureable conversion of 3  $\rightarrow$  4 was observed (glc analysis) in 4 hr. The calculated quantum yield for isomerization was  $0.013 \pm 0.004$ .



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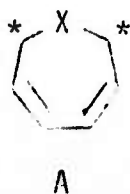
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Figure. Potential energy surfaces for the photochemical and thermal interconversions of 3 and 4.  $\Delta H^\ddagger(4 \rightarrow 3, 128^\circ) = 27 \text{ kcal/mol}$ .