

proton resonances is based on the fact that BPR maintains the syn and anti relationship of methylene protons with respect to NO. The ST permutation does not show this behavior (Scheme I), and it is thus possible to identify the permutational sequence responsible for the rearrangement. The necessary structural information can be extracted from an analysis of the vicinal proton-proton coupling constants using the Karplus equation. It is first necessary to average  ${}^3J_{\text{HH}}$  over the two rapidly equilibrating<sup>8</sup> conformations of the puckered five-membered ring; this yields two values,  $J = J(\varphi)$  and  $J' = \frac{1}{2}[J(120 + \varphi) + J(120 - \varphi)]$  where  $\varphi$  is the dihedral PCCP angle. Karplus equation parameters appropriate to coordinated ethylenediamine<sup>9</sup> show that  $J$  is smaller than  $J'$  by  $\sim 2$  Hz. BPR predicts a pattern of two  $J$  (small) and one  $J'$  (large), while ST would show just the opposite pattern. The actual pattern is in agreement only with BPR, a simultaneous motion of two axial and two equatorial phosphorus nuclei.

It is evident that BPR interconverts enantiomers while ST does not. We have attempted to confirm our assignment of BPR by determining whether enantiomerization and axial-equatorial interchange occur at identical rates using  ${}^{31}\text{P}$  nmr in the presence of chiral shift reagents.<sup>10</sup> However, the low basicity of the nitrosyl oxygen combined with the limited solubility of  $\text{RuNO}(\text{diphos})_2\text{BPh}_4$  in  $\text{CHCl}_3$  makes complex formation negligible; the  ${}^{31}\text{P}$  resonance is unaffected by shift reagents.

If the permutational sequence which occurs in these complexes proceeds by a Berry physical pathway, the transition state is a square pyramid with NO axial. Bending of the MNO angle may therefore accompany pseudorotation and have an observable effect upon the activation energy. We are attempting to assess the importance of this effect by studying the energetics of pseudorotation in other complexes of the type  $\text{ML}(\text{diphos})_2$ ,  $\text{L} = \text{NO}$  and  $\text{CO}$ .

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(8) We have established ring puckering to be rapid in diphos complexes with a variety of coordination geometries. J. S. Miller, unpublished results.

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(10) G. Whitesides and D. Lewis, *J. Amer. Chem. Soc.*, **93**, 5915 (1971).

P. R. Hoffman, J. S. Miller  
C. B. Ungermann, K. G. Caulton\*

Contribution No. 2319  
Department of Chemistry, Indiana University  
Bloomington, Indiana 47401

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## Mechanisms of Photochemical Reactions in Solution. LXXVI.<sup>1</sup> Complex Decay Mechanisms in Bi- and Trichromophoric Systems

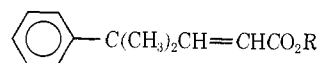
Sir:

Bichromophoric molecules, in which the chromophoric units are not directly conjugated, have been

(1) Part LXXV: F. A. Carroll and G. S. Hammond, *Isr. J. Chem.*, **10**, 613 (1972).

studied extensively by photochemists and spectroscopists.<sup>2-19</sup> Appearance of new, red-shifted emission<sup>20-22</sup> and accelerated nonradiative decay by both chemical and nonchemical paths give evidence for decay of excited states by way of low-lying states involving excitation delocalization over the two chromophoric units, even when absorption spectra show no significant evidence for interchromophoric coupling in excitation.

Although bichromophoric systems are far from understood, we have begun to probe the behavior of "polychromophoric" molecules in which three or more chromophoric units are potentially capable of participating in excitation delocalization. We wish to report the behavior of the bichromophoric system **1** and that of trichromophoric molecules **2** and **3** in which aliphatic and aromatic amino functions have been added as third chromophoric units.



- 1, R =  $\text{C}_2\text{H}_5$
- 2, R =  $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
- 3, R =  $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}_6\text{H}_5$

All three systems consist of cis and trans isomeric pairs. The trans isomers were prepared by standard synthetic methods in which the key step was addition of the anion derived from diethyl carboxymethylphosphonate to phenyldimethylacetaldehyde.<sup>23</sup> In all cases irradiation led to trans  $\rightarrow$  cis isomerization and in some cases other changes (*vide infra*). The cis isomers were then isolated by vapor chromatography. The compounds were characterized by nmr and uv spectra.

The absorption spectra of cis- and trans-**1** were similar to that of cumene in the 260-nm region but with small red shifts and small increases in total intensity. In both cases there is much stronger absorption in the region below 250 nm which does not reach a maximum above 210 nm. The latter feature qualitatively resembles the spectrum of ethyl crotonate but with a

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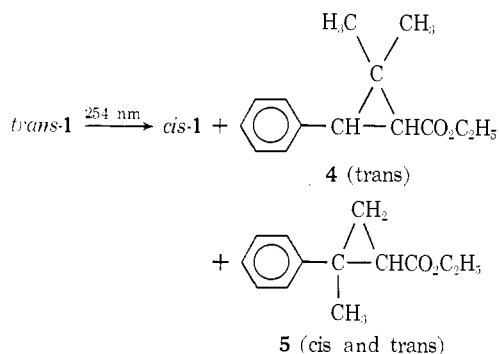
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(23) W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

large red shift. We believe that this absorption must be due to direct excitation to a delocalized excited state formed by mixing of arene-localized states, derived from the  $E_{1u}$  or  $B_{1u}$  states of benzene, with the  $N \rightarrow V$  transition of the unsaturated ester group. The isomers of **2** have similar spectra with observable second maxima in the near uv (trans, 204 nm,  $\epsilon$  26,260 and cis, 205 nm,  $\epsilon$  19,395). In the cis isomer the tail of the strong, featureless absorption band is pushed to sufficiently long wavelength to nearly obliterate the usual vibronic features of the long wavelength band, so that the usual maxima appear only as shoulders. The isomers of **3** show three maxima in the near-ultraviolet. The first (trans, 299 nm,  $\epsilon$  1682 and cis, 298 nm,  $\epsilon$  1635) and second (trans, 252 nm,  $\epsilon$  18,260 and cis, 252 nm,  $\epsilon$  17,327) are similar in intensity and positions to maxima in the spectrum of *N,N*-dimethylaniline. The third (trans, 202 nm,  $\epsilon$  37,330 and cis, 203 nm,  $\epsilon$  39,231) could be associated either with the strong absorption bands of **1** and **2**, with the third band of dimethylaniline, or both.

Neither of the isomers of **1** or **2** shows detectable fluorescence. However, both isomers of **3** show emission with maxima at 330 nm (trans,  $\phi_f \cong 0.001$  and cis,  $\phi_f \cong 0.0025$ ) similar in band shape and position but much weaker than the emission from dimethylaniline ( $\Phi_f = 0.11$ ).<sup>24</sup>

Irradiation of *trans*-**1** in hexane solution with a 254-nm lamp resulted in rapid formation of *cis*-**1** (initial  $\phi = 0.36$ ) and slow formation of two new compounds, **4** and **5**, which were identified by nmr spectra and independent synthesis.<sup>25,26</sup> Irradiation of *cis*-**1** under the



same conditions leads to fairly rapid formation of *trans*-**1** ( $\phi = 0.14$ ) and slow formation of both isomers of **5**. Termination of the irradiation of *trans*-**1** at low conversion shows only production of *cis*-**1** and *trans*-**4**, indicating that **5** arises only from *cis*-**1**. Initial quantum yields for skeletal rearrangement reactions of the two isomers are approximately 0.02 although precision measurements are difficult because of early appearance of products formed from the geometrical isomer not initially present.

(24) Data of I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965 corrected as recommended by J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970.

(25) The isomers of **4** were prepared by the method of J. Farkaš, P. Kouřim, and F. Šorm, *Chem. Listy*, **52**, 695 (1958); *Chem. Abstr.*, **52**, 13651 (1958).

(26) A mixture of isomers of **5** was prepared by reaction of ethyl diazoacetate with  $\alpha$ -methylstyrene.<sup>27</sup> Samples of the pure isomers were separated by preparative vapor chromatography but unequivocal structural assignments have not been made.

(27) For conditions see R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 7405 (1969).

Molecular rearrangement of *trans*-**1** is of the type previously encountered<sup>6</sup> in which stereospecific 1,2 migration of a phenyl group occurs from an excited singlet state of the system. The rearrangement of *cis*-**1** is analogous to photoreactions of  $\alpha,\beta$ -unsaturated esters.<sup>28</sup> The reaction is believed to involve abstraction of a  $\delta$  hydrogen from one of the methyl groups followed by ring closure.

Although we have no direct proof of the point, we are tempted to assign *cis*  $\rightleftharpoons$  *trans* isomerization exclusively to triplets since the process is the only photo-reaction observed using acetone as a sensitizer and irradiating with 313 nm light. This *cis*/*trans* ratio at the stationary state is 0.61. If the triplet hypothesis for the direct excitation is correct, the triplet yield from *trans*-**1** can be estimated as 0.9. Since this yield is higher than is commonly observed with alkylbenzenes,<sup>15,29</sup> intersystem crossing may occur after relaxation to a delocalized excited singlet state. The same line of reasoning would indicate that the yield of triplets from *cis*-**1** is only 0.23, indicating that this isomer undergoes extensive radiationless decay from excited singlets. This process may involve  $\delta$  hydrogen abstraction followed by thermal reversion of the abstracted atom to its original site, a process familiar in the photochemistry of aliphatic ketones.<sup>30,31</sup>

Irradiation of either *cis*- or *trans*-**2** with 254-nm light leads to rapid geometric isomerization and to slow formation of many new products. Those which have been identified by vapor chromatography and mass spectrometry are methyl 4-methyl-4-phenyl-2-pentenoate, 5-methyl-5-phenyl-3-hexenone, 4,4-dimethyldihydronaphthone-1, 3-methyl-3-phenyl-1-butene, 1,1-dimethylindene, 2-phenylpropane, and 2-phenylpropene. Still other products are formed in miniscule amounts. However, a surprising change in the photochemistry has occurred on introduction of the dimethylamino group since the new products can be attributed to mechanisms involving breaking of nearly every bond in the side chain. The initial quantum yields for geometric isomerization are smaller ( $\phi_{t \rightarrow c} = 0.24$  and  $\phi_{c \rightarrow t} = 0.079$ ) than for the **1** system. Attempts to study isomerization by ketonic sensitizers were foiled by appearance of many side reactions, probably arising from interaction of the excited carbonyl compounds with the amino function.<sup>32</sup>

In comparison with either **1** or **2**, the **3** system is remarkably photochemically stable. Although traces of other products were formed, the only significant change on irradiation in hexane was *cis*-*trans* isomerization and the system could be brought to a photostationary state with very little loss of material. The initial quantum yields are  $\phi_{t \rightarrow c} = 0.31$  and  $\phi_{c \rightarrow t} = 0.30$ , in excellent agreement with the stationary-state ratio of  $1.00 \pm 0.03$ . Identical results were obtained on irradiation at 254 and 313 nm.

We believe that excitation of either *cis*- or *trans*-**1** is followed by relaxation, before fluorescence can occur, to delocalized excited states. The delocalized states must then decay by two paths, one leading to geometric

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(32) P. J. Wagner and T. Jellinek, *ibid.*, **93**, 7328 (1971), and earlier papers in the series.

isomerization and another leading to chemical and/or nonchemical radiationless decay. The remarkable effect of the dimethylamino group in **2** shows that this group surely must play a role in controlling the course of nonradiative decay of any state formed by interaction between the phenyl and unsaturated ester chromophores. We have no explanation for the apparent fact that the interaction should divert internal conversion so as to produce such a multitude of bond-breaking processes.

Light absorption by **3** must produce states with the excitation largely localized in arylamino group. That these states must have finite lifetimes is shown by the weak fluorescence. We suspect that the fluorescent state decays mainly by internal energy transfer to a delocalized state similar to that postulated for **1**. If so, decay of that state must be guided by the *N*-methyl-anilino group since the usual skeletal rearrangements disappear completely, or nearly so. Sixty-one per cent of the energy put into the molecules can be accounted for by geometric isomerization (triplet path?), so some 40% must be attributed to other nonradiative decay processes. These in turn may be related to quenching of fluorescent states of aromatic compounds by amines<sup>33</sup> although no long wave-emission similar to that seen with naphthalene derivatives having amino groups<sup>20</sup> attached to side chains has been observed.

We conclude that excitation decay in molecules containing several chromophoric units may involve complex interaction among all the groups in the system.

**Acknowledgment.** This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, under Contract No. 71-1958, and the Belgian Foundation for Scientific Research.

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(34) NATO Postdoctoral Research Fellow, 1971-1972.

(35) National Research Council of Canada Research Fellow, 1968-1971.

(36) Author to whom inquiries should be addressed at the Division of Natural Sciences, University of California, Santa Cruz, Calif. 95060.

D. DeKeukeleire,<sup>34</sup> E. C. Sanford,<sup>35</sup> G. S. Hammond\*<sup>36</sup>

Contribution No. 4645

Gates and Crellin Laboratories of Chemistry

California Institute of Technology

Pasadena, California 91109

Received March 23, 1973

### Photoisomerization of Phenalen-1-one Oxide. The Absence of $\alpha$ -Hydrogen Exchange in the Alkaline Peroxide Epoxidation of $\alpha,\beta$ -Unsaturated Ketones<sup>1</sup>

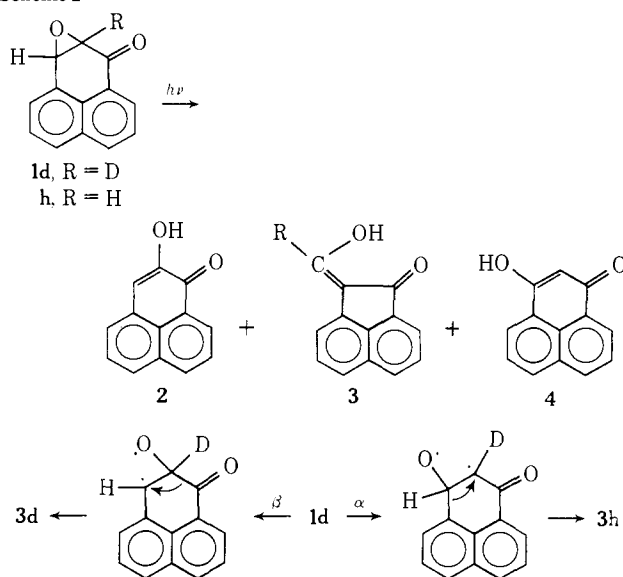
Sir:

Irradiation (>280 nm) of phenalen-1-one oxide (**1h**) in acetonitrile yields 2-hydroxyphenalen-1-one (**2**), acenaphthen-1-one-2-carboxaldehyde (**3h**), and 3-hydroxyphenalen-1-one (**4**) in approximately 30, 16, and 5% yields, respectively.<sup>2</sup> Whereas the formation of **2** and **4** are suggestive of initial  $C_{\beta}$ -O and  $C_{\alpha}$ -O bond scission, respectively, followed by hydrogen migration, **3** may arise from either biradical intermediate. On the other hand, irradiation of **1d** is expected to provide **3h**

(1) Taken from the Ph.D. Thesis of L. Q. B., North Dakota State University, 1972.

(2) S. P. Pappas, R. M. Gresham, and M. J. Miller, *J. Amer. Chem. Soc.*, **92**, 5797 (1970).

Scheme I



by the  $\alpha$  pathway and **3d** via  $\beta$  cleavage (Scheme I). Herein, we report on the synthesis and photorearrangement of **1d** which establish that (1)  $C_{\beta}$ -O bond cleavage precedes ring contraction to **3** and (2)  $\alpha$ -H (D) exchange does not accompany alkaline peroxide epoxidation of  $\alpha,\beta$ -unsaturated ketones.

We anticipated that alkaline peroxide epoxidation<sup>3</sup> of **5h** in deuteriated media would provide **1d** directly as a consequence of  $\alpha$ -D exchange via the enolate adduct **6** which was expected to compete favorably with ring closure (Scheme II). Indeed, the pseudo-first-order rate constant for proton transfer from water to the  $\alpha$ -C of an enolate ( $pK_a = 20$ ) may be estimated to be on the order of  $10^5 \text{ sec}^{-1}$ .<sup>4</sup> However, epoxidation of **5h** with alkaline deuterium peroxide yielded **1h** (60% yield);<sup>5</sup> no deuterium incorporation was in evidence by nmr and mass spectrometry. Analogous results were obtained with benzalacetophenone. As expected, epoxidation of  $\alpha$ -deuterio-phenalen-1-one (**5d**)<sup>6</sup> in protiated media<sup>5</sup> provided the desired epoxy ketone, **1d**. Apparently,  $\alpha$ -H (D) exchange of the product does not occur under these conditions,<sup>5</sup> although exchange has been observed with sodium ethoxide catalysis.<sup>7</sup>

Previous studies have established that alkaline peroxide epoxidation is highly stereoselective in that, irrespective of the geometry of the  $\alpha,\beta$ -unsaturated ketone, the product with the less hindered carbonyl group is kinetically favored.<sup>8</sup> These results implicate

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(4) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964). This reference provides the rate constant for the reverse process of proton transfer from the  $\alpha$ -C of a ketone (acetone) to hydroxide ion ( $2.7 \times 10^{-1} M^{-1} \text{ sec}^{-1}$ ), from which the desired rate constant may be obtained as discussed on p 10.

(5) The alkaline peroxide solution was prepared by adding 7.0 g of sodium peroxide to 30 ml of deuterium oxide (or water) with cooling, allowing the mixture to stand for 3 hr at room temperature, and filtering. The resulting solution contained approximately 5% peroxide. A 10-ml aliquot was slowly added to 1.0 g of the  $\alpha,\beta$ -unsaturated ketone in 30 ml of dioxane at 50°. After 1 hr, the solution was partitioned between chloroform and water; and, after drying, the chloroform solution was evaporated to dryness. The residue, which contained substantial amounts of starting ketone, was resubjected to the same conditions two or three additional times to afford pure epoxy ketone after recrystallization.

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