**Table I.** The Configurational Isomerization of *trans*-Stilbene (II) and Fumaronitrile (IV) Induced by Irradiation of the Charge-Transfer Complex[a]

| *t*, h | I, % | II, % | III, % | IV, % |
|---|---|---|---|---|
| 0 | | 100 | | 100 |
| 5 | 75 | 25 | 6 | 94 |
| 27 | 80 | 20 | 17 | 83 |
| 45 | 82 | 18 | 22 | 78 |
| 97 | 78 | 22 | 32 | 68 |
| 208 | 73 | 27 | 40 | 60 |
| 279 | 72 | 28 | 40 | 60 |
| (200 | 25 | 75)[b] | | |
| (209 | 86 | 14 | 11 | 89)[c] |

[a] Starting with a degassed benzene solution of II (0.2 M) and IV (0.2 M) at 10 °C. The irradiation source was a 450-W medium-pressure mercury vapor lamp (Hanovia) through chemical solution filter A (see Figure 1b). Similar results were obtained using acetonitrile as solvent. [b] Same conditions as in footnote *a* except in the absence of the dinitrile. This is the photostationary state under these conditions. [c] Same conditions as in footnote *a* except a Corning glass filter (0-51) was used (see Figure 1b).

photostationary state rich in II; IV is not isomerized under these conditions.

We believe the isomerization of both the stilbenes and the dinitriles involves their triplet states, formed, at least in part, by a deactivation pathway of the excited state of the charge-transfer complexes. One possible mechanism for formation of the triplets is a triplet exit channel of the geminate radical-ion pair.[2] An estimate of the energy available within the geminate radical-ion pair, based upon the oxidation potential of the donors and the reduction potential of the acceptors, indicates that formation of the triplets of I-IV would be spontaneous.[5] Evidence consistent with this mechanism is the observation of photochemically induced dynamic nuclear polarization (CIDNP) enhanced absorption of the vinyl protons of I when an acetonitrile-$d_3$ solution of II and IV is irradiated in the $^1$H NMR spectrometer.[6]

These results contrast markedly with a recent report, by Lewis and Johnson, on the photochemical reaction between *trans*-stilbene and dimethyl fumarate.[7] A major reaction with the diester in benzene was cycloaddition, while isomerization of the *trans*-stilbene was attributed to direct excitation. However, we observe similar CIDNP of I (acetonitrile-$d_3$ solution) in this case as well; at least part of the stilbene isomerization must occur by the triplet exit channel of the geminate radical-ion pair. Also related to these results is an early report of the observation of CIDNP emission of the vinyl protons of III, upon irradiation of the naphthalene-IV system.[8] The fact that we do not observe emission from III upon irradiation of II-IV is not surprising in view of the relative inefficiency of the isomerization of IV.

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(1) Contribution No. 203 from the Photochemistry Unit.

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(4) For I-IV, $K^{AO} = 0.044 \pm 0.005\ M^{-1}$; $\epsilon^{358}$ 333, $\epsilon^{360}$ 250, $\epsilon^{362}$ 167. For II-IV, $K^{AO} = 0.17 \pm 0.05\ M^{-1}$; $\epsilon^{356}$ 776, $\epsilon^{360}$ 657, $\epsilon^{362}$ 577.

(5) The energy of the geminate radical-ion pair of II-IV is 63 kcal mol$^{-1}$, estimated from 23.06 ($E^{ox}_{1/2}$(D) − $E^{red}_{1/2}$(A)): D. Rehm and A. Weller, *Isr. J. Chem.* *8*, 259 (1970). The triplet energies of I ($E_T$ = 57 kcal mol$^{-1}$) and II ($E_T$ = 49 kcal mol$^{-1}$) have been reported: G. S. Hammond et al., *J. Am. Chem. Soc.*, **86,** 3197 (1964). $E^{ox}_{1/2}$(II) = 1.10 V (vs. Ag/Ag$^+$): J. E. Kuder, H. W. Gibson, and D. Wychick, *J. Org. Chem.*, **40,** 875 (1975). The triplet energy of III and IV ($E_T$ = 50 kcal mol$^{-1}$) and $E^{red}_{1/2} = -1.63$ (vs. Ag/Ag$^+$) for both III and IV: P. C. Wong and D. R. Arnold, *Can. J. Chem.*, in press.

(6) According to the modified Kaptein rule (G. L. Closs and M. S. Czeropski, *J. Am. Chem. Soc.*, **99,** 6127 (1977); J. Bargon, *ibid.*, *99*, 8351 (1977)), $\Gamma_{nl} = \mu \cdot \epsilon \cdot a_i \cdot \Delta g \cdot \gamma = +$: enhanced absorption for α-H of I formed from II-IV, $\mu = -$ (singlet), $\epsilon = +$ (cage), $\Delta g = 2.002 - 2.004 = -$, $a(\alpha\text{-H}) = -$, $\gamma = -$ (exit to triplet).

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(9) Address correspondence to this author, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3.

**Donald R. Arnold,*[9] Po Cheong Wong**

*Photochemistry Unit, Department of Chemistry*
*The University of Western Ontario*
*London, Ontario, Canada, N6A 5B7*

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## Concerning the Diene-Induced Photodechlorination of Chloroaromatics[1]

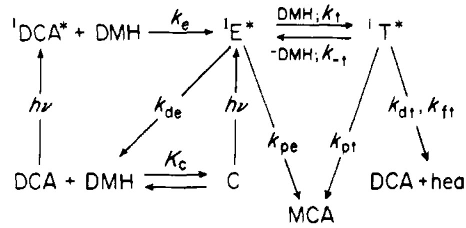
*Sir:*

In contrast to the amine-enhanced reaction,[2-4] few diene-haloaromatic photodehalogenations have been reported[3] and the salient features of this transformation remain undisclosed. We present evidence indicating that photodechlorination in the 9,10-dichloroanthracene (DCA)-2,5-dimethyl-2,4-hexadiene (DMH) system[5-7] in acetonitrile (i) is a consequence of exciplex and triplex formation, (ii) involves protonation rather than hydrogen abstraction, and (iii) proceeds through long-lived ion radical intermediates.[8a]

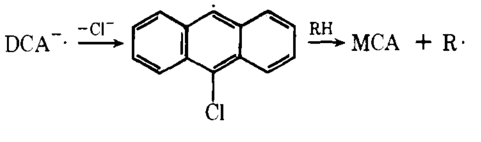
Irradiation (404 nm) of DCA in degassed acetonitrile containing DMH affords 9-chloroanthracene (MCA)[8b] and diene related products. At wavelengths where MCA absorbs (λ <395 nm), anthracene formation is observed from solutions irradiated to high conversions.

Scheme I provides the simplest mechanism consistent with spectroscopic measurements[7] and quantum yields for DCA loss ($\phi_{-DCA}$).[8b,c] Rate constants for formation and decay of the DCA-DMH singlet exciplex ($^1E^*$) and DCA-2DMH singlet triplex ($^1T^*$) in acetonitrile have been discussed.[7] Detailed treatment of $\phi_{-DCA}$ dependence on [DMH] gives $k_e\tau_m = 92 \pm 7\ M^{-1}$ at 30 °C in good agreement with $k_e\tau_m$ values of 106 and 89 $M^{-1}$ obtained from steady-state and transient fluorescence data,[7] respectively.[9] Remarkably, triplex formation does not alter the efficiency of MCA production ($k_{pe}\tau_e = 0.24$ vs. $k_{pt}\tau_t/(1 - k_{-t}\tau_t) = 0.25$, where $\tau_e$ and $\tau_t$ are exciplex and triplex lifetimes, respectively).

Scheme I. MCA Formation in Degassed Acetonitrile



Direct dechlorination within $^1E^*$ is unlikely since inefficient cycloaddition rather than MCA formation occurs in nonpolar media.[6b] Dissociation of $^1E^*$ to ion radicals[10] (DCA$^-\cdot$ and DMH$^+\cdot$) provides a pathway to MCA, eq 1, in accord with that generally postulated for quencher-induced photodehaloge-



(1)

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**Table I.** Deuterium Incorporation and Oxygen Quenching, 30 °C

| $D_2O$[a] | | | oxygen[b] | | |
|---|---|---|---|---|---|
| | | | | % DCA loss | |
| $[D_2O]$, M | $\phi_{-DCA}$[c] | % MCA-$d_1$[d] | [DMH], M | degassed | air satd |
| 0.00 | 0.057 | | 0.23 | 21 | 5.0 |
| 0.055 | 0.057 | 84 | 0.12 | 20 | 1.1 |
| 0.14 | 0.058 | 91 | 0.097 | 19 | 0.4 |
| 0.28 | 0.055 | 95 | 0.075 | 20 | 0.0 |
| 0.55 | 0.057 | 97 | 0.034 | 17 | 0.0 |
| 1.4 | 0.056 | | 0.011 | 11 | 0.0 |

[a] Degassed solutions, $[DCA] = 5 \times 10^{-4}$ M, $[DMH] = 3.5 \times 10^{-3}$ M. [b] From solutions irradiated (404 nm) in parallel, $[DCA] = 4 \times 10^{-4}$ M. [c] Irradiated at 366 nm to 11% conversion. [d] Irradiated to ~95% conversion at 404 nm. MCA was isolated by TLC and analyzed for deuterium content by mass spectroscopy.

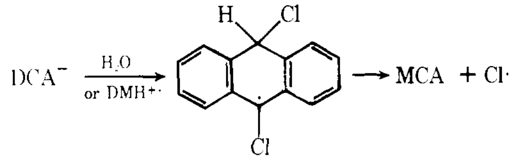
**Table II.** Deuterium Incorporation under Anhydrous Conditions[a]

| solvent | diene | % MCA-$d_1$[b] |
|---|---|---|
| $CH_3CN$ | DMH-$d_{12}$ | 50 |
| $CD_3CN$ | DMH-$d_{12}$ | 60 |
| $CD_3CN$ | DMH | 30 |

[a] Degassed solutions at 30 °C, $[DCA] = 8 \times 10^{-4}$ M, $[\text{diene}] = 1 \times 10^{-2}$ M. Solvent and diene were dried ($CaH_2$) and handled under vacuum. [b] See footnote *d* in Table I.

nations.[2,3] While our observations implicate $DCA^{-}\cdot$, they do not support the free-radical pathway in eq 1.

Deuterium incorporation results using $CH_3CN$-$D_2O$ appear in Table I, where MCA-$d_1$ is 9-chloroanthracene-*10-d*. Except under rigorously anhydrous conditions, Table II, attempts to effect deuteration from $CD_3CN$ or DMH-$d_{12}$[11] failed. From these findings, it is evident that displacement of chlorine is a consequence of protonation and not hydrogen-atom abstraction.[12,13] Furthermore, since $D_2O$ affects product structure but not the efficiency of DCA loss, Table I, all anion radicals formed give MCA regardless of the proton source. In anhydrous $CH_3CN$ predominant protonation by $DMH^{+}\cdot$ is inferred, Table II, eq 2.



(2)

Spectroscopic observations in the presence of air rigorously exclude significant oxygen quenching of MCA formation owing to interception of any excited singlet state.[7] On the other hand large oxygen quenching effects can be accounted for if the longer-lived[14] $DCA^{-}\cdot$ is the MCA precursor since electron transfer from $DCA^{-}\cdot$ to oxygen is expected to be diffusion controlled ($E_{1/2}(R/R^-) \simeq -1.5$ and $-0.57$ V vs. SCE for DCA[15] and $O_2$,[16] respectively).[13b] Consistent with this mechanism, 1,2,4,5-tetracyanobenzene ($E_{1/2}(R/R^-) = -0.64$ V vs. SCE),[17] $10^{-3}$ M, also suppresses DCA loss. The known slow protonation of the anthracene anion radical[13b] and the effects of low concentrations of proton donors and quenchers (Tables I, II) are consistent with a minimum $DCA^{-}\cdot$ lifetime in the microsecond range.[14] The decreasing $O_2$ quenching efficiency above 0.1 M DMH, Table I, can be ascribed to $O_2$ scavenging by the diene.[16-18] Photodehalogenations occurring directly within the exciplex are insensitive to $O_2$.[4a-c]

Since spectroscopic observation of radical ions from olefin-arene exciplexes is lacking, this work strongly supports proposed mechanisms in several systems,[16,17,19] particularly those concerning olefin photooxidation[16] and photocycloaddition of methyl 1,2-diphenylcyclopropene-3-carboxylate to 9,10-dicyanoanthracene.[17]

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**William K. Smothers, Kirk S. Schanze, Jack Saltiel***
*Department of Chemistry, Florida State University*
*Tallahassee, Florida 32306*

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## Aggregation in Strong Acid. A Micelle of Carbonium Ions

*Sir:*

Arnett et al. recently reported that a long-chain aliphatic amide, *N*-$\alpha$-methylbenzylstearamide, forms monolayers on subphases composed of 15-50% $H_2SO_4$.[1] Racemic and (*S*)-(−) amide were shown to have different surface tension vs. [acid] curves. We describe here the behavior of a long-chain amide and related compounds in 70-95% $H_2SO_4$ where aggregation, not monolayer formation, predominates. During the course of this work, a micelle of carbonium ions was observed for the first time.