We are currently investigating the present desulfurizative stannylation and its applications to organic synthesis.[19]

References and Notes

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(4) H. G. Kuivila, *Synthesis*, 499 (1970); *Acc. Chem. Res.*, **1**, 299 (1968).
(5) Compound **1** was easily prepared by the reaction of propargyl bromide and 2-mercaptobenzothiazole in the presence of triethylamine (or 2-mercaptobenzothiazole sodium salt) in acetone: mp 45.1–45.6 °C (from EtOH).
(6) The benzothiazole moiety was trapped by tri-*n*-butyltin hydride to produce 2-(tri-*n*-butylstannylthio)benzothiazole (see Scheme I).
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(9) In this case, 2-mercaptobenzothiazole (**4**) was also isolated in 39% yield.
(10) K. Hirai and K. Kishida, *Tetrahedron Lett.*, 2117 (1972).
(11) In this case, the complete separation of stannylallene **2** from the byproducts was difficult by simple distillation.
(12) The structures of the products from dithiocarbamate **9** or sulfone **10** are now under investigation, although the cleavage of sulfone was clearly observed in the case of the compound **10**.
(13) E. J. Corey and R. H. Wollenberg, *J. Org. Chem.*, **40**, 2265 (1975).
(14) J. L. Kice in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 24.
(15) W. P. Newmann and J. Schwindt, *Chem. Ber.*, **108**, 1339, 1346 (1975); e.g., $RS\cdot + R_3'SnH \rightarrow RSH + R_3'Sn\cdot$, $RSH + R_3'SnH \rightarrow RS\text{-}SnR_3' + H_2$.
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(19) In contrast to the propargyl sulfone **10**, allylic sulfones were found to react with tri-*n*-butyltin hydride to produce allyltin compounds via an S_H' process. The details of this allyl transfer will be reported in near future.

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Radical Ions in Photochemistry. 7. Configurational Isomerization of Alkenes Induced by Irradiation of Charge-Transfer Complexes[1]

Sir:

Photophysical studies have firmly established that one of the deactivation pathways of excited charge-transfer complexes and exciplexes can lead to the triplet of either (or both) the component donor or acceptor.[2] This phenomenon is potentially useful for photochemistry since the factors controlling formation of the triplet are not directly dependent upon the decay processes of the individual components of the complex, nor upon the rate of energy transfer as is photosensitization (triplet–triplet transfer). We report here the first example of a configurational isomerization which involves the triplet of an olefin, where the photostationary state is dependent upon the absorption spectra of the charge-transfer complexes involving the individual isomers.

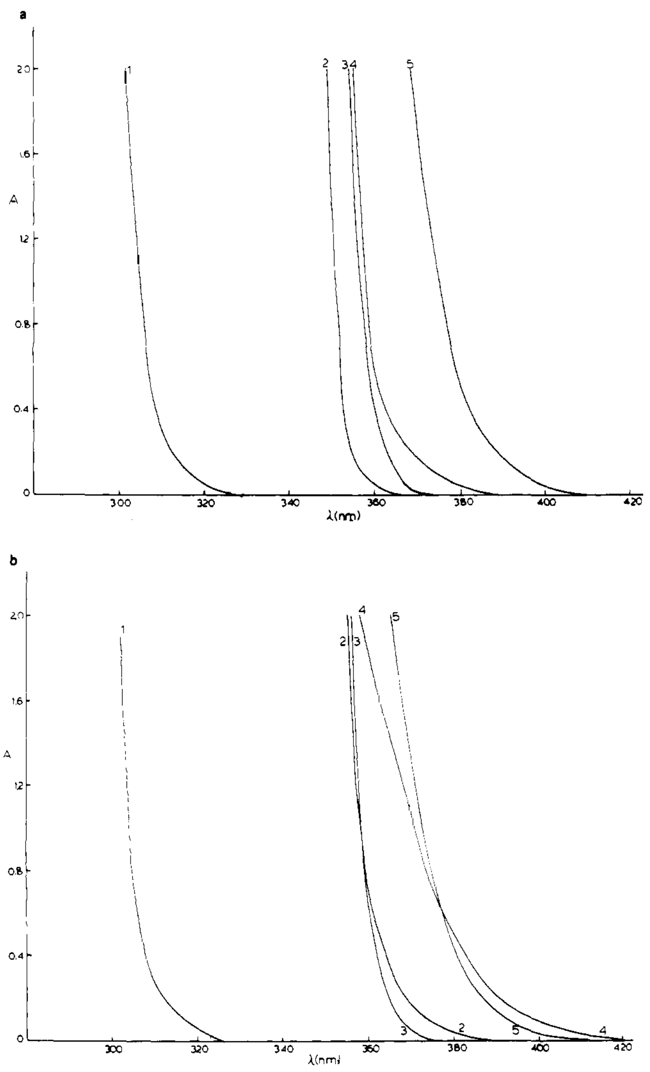

Figure 1. a, (1) 0.2 M IV, (2) 0.2 M II, (3) 0.2 M I, (4) 0.2 M I + 0.2 M IV, (5) 0.2 M II + 0.2 M IV (benzene solution); b, (1) 0.2 M III, (2) 0.2 M I + 0.2 M III, (3) filter solution A, 1 cm (1 g of $BiCl_3$ in 150 mL of 10% HCl), (4) Corning glass filter 0-51, (5) 0.2 M II + 0.2 M III (benzene solution).

The long-wavelength absorption curves of the donors, *cis*- and *trans*-stilbene (I and II), and the acceptors, maleonitrile (III) and fumaronitrile (IV), and the charge-transfer complexes involving these components, are shown in Figure 1. We call particular attention to differences in the curves for the complexes between *cis*- and *trans*-stilbene and fumaronitrile (Figure 1a). An analysis of the variation in these spectra as a function of fumaronitrile concentration indicates that the difference in these two curves is the result of both a larger association constant and extinction coefficient for the II–IV than for the I–IV complex.[3,4]

Irradiation of a degassed benzene solution of *trans*-stilbene (II, 0.2 M) and fumaronitrile (IV, 0.2 M) in the region of the charge-transfer transition ($\lambda > 356$ nm) leads predominantly to isomerization of both the stilbene and the dinitrile; other photochemical reactions are relatively unimportant. The progress of the isomerizations can be followed by vapor-phase chromatography (VPC) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy and the isomeric compositions, as a function of irradiation time, are summarized in Table I.

The isomerization of the *trans*-stilbene is more efficient than that of the dinitrile and the mixture attains a maximum (>80%) composition of *cis*-stilbene. Continued irradiation leads to a decrease in the *cis*- to *trans*-stilbene ratio as the fumaronitrile isomerizes to maleonitrile. Prolonged irradiation (10 days) gives the photostationary state, which is also obtained starting with I and IV. An even higher ratio (I/II, 6) of *cis*-stilbene can be attained if a light filter which cuts off irradiation of longer wavelengths ($\lambda > 360$ nm) is used, although the isomerization is much slower since less light is absorbed under these conditions. Notice, in Figure 1a, that both I and II absorb beyond the cut-off of filter A ($\lambda > 356$ nm). Prolonged irradiation of II under these conditions causes isomerization to a

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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}; ϵ^{358} 333, ϵ^{360} 250, ϵ^{362} 167. For II–IV, $K^{AO} = 0.17 \pm 0.05$ M^{-1}; ϵ^{356} 776, ϵ^{360} 657, ϵ^{362} 577.

(5) The energy of the geminate radical–ion pair of II–IV is 63 kcal mol^{-1}, estimated from 23.06 ($E_{1/2}^{ox}$(D) − $E_{1/2}^{red}$(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). $E_{1/2}^{ox}$(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 $E_{1/2}^{red}$ = −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($\alpha$-H) = −, $\gamma = -$ (exit to triplet).

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Concerning the Diene-Induced Photodechlorination of Chloroaromatics[1]

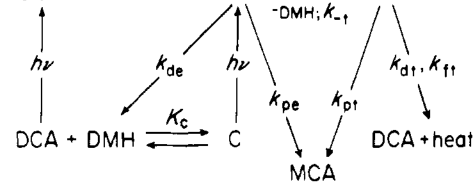
Sir:

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]

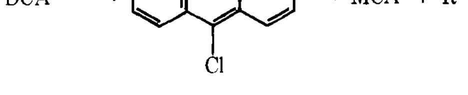
Irradiation (404 nm) of DCA in degassed acetonitrile containing DMH affords 9-chloroanthracene (MCA)[8b] and diene related products. At wavelengths where MCA absorbs (λ <395 nm), anthracene formation is observed from solutions irradiated to high conversions.

Scheme I provides the simplest mechanism consistent with spectroscopic measurements[7] and quantum yields for DCA loss (ϕ_{-DCA}).[8b,c] Rate constants for formation and decay of the DCA–DMH singlet exciplex (^{1}E*) and DCA–2DMH singlet triplex (^{1}T*) in acetonitrile have been discussed.[7] Detailed treatment of ϕ_{-DCA} dependence on [DMH] gives $k_e\tau_m$ = 92 ± 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 τ_e and τ_t are exciplex and triplex lifetimes, respectively).

Scheme I. MCA Formation in Degassed Acetonitrile



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



(1)

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